

Preservation of murals with electrokinetic – with focus on desalination of single bricks

Inge Rörig-Dalgaard



Conservation of murals should not be based on logical fantasies (as on the frontpage) as a consequence of extensive salt deteriorated murals

Contrary, the aim is to extract the damaging salt and reduce conservation to minor refreshments

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Inge Rörig-Dalgaard

Ph.D. Thesis

Department of Civil Engineering
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Preface

This PhD thesis is submitted in completion of the requirements for the PhD degree at the Technical University of Denmark (DTU). The work was funded by “Realdania” and “Villum Kann Rasmussen Fonden” and was made in the friendly and inspiring environment in the section for Building Materials, DTU. The supervisors were associated professor Lisbeth M. Ottosen and associated professor Kurt Kielsgaard Hansen, both Department of Civil Engineering, DTU. They are both acknowledged for their guidance and comments.

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However, at the end of the day the people with whom you share all facets of the day is the family. For this I warmly want to thank my bellowed husband Martin and our wonderful daughters Anne-Sofie and Juliane.

Inge Rörig-Dalgaard
October 2008

Summary

At present there is a lack of effective salt extraction methods for treatment of painted brick masonry vaults containing salts. In the case of deterioration of murals repainting is carried out. Since the source for the deterioration is not removed, the deterioration-repainting cycle continues. In case of extensive deterioration of larger areas repainting might be impossible.

The present thesis is based on the idea of using the electrokinetic phenomena's to accelerate and obtain an effective desalination of brick masonry for preservation of murals. A phenomenon's which previously has showed its effect in fine grained and porous materials.

The present study aimed to document the electrokinetic desalination effect, identify side effects and optimize the process on brick masonry in connection with painted surfaces (murals).

The investigations were divided into:

- characterization of bricks
- description of fundamental electrokinetic effects in bricks
- optimization of the electrokinetic setup
- electromigration in pilot scale
- examination of the salt deterioration cause in praxis

Characterization of bricks

The characterization of bricks was made, both regarding the amount of soluble ions and pH in relation to the environmental influence and the influence of brick firing temperatures on the pore system. This separation was carried out to separate the ionic content and the pore systems influence on the electrokinetic induced transport processes.

Brick masonry is affected by different environmental factors e.g. acidic rain. The effect of the exposure on bricks was investigated on a variety of bricks: new & old (related to location and exposure), red & yellow and manufactory procedure (tunnel oven, circular kiln). The effect and extend from environmental influence as e.g. acidic rain was measurable on the amount of soluble ions and pH.

Preparation of brick and clinker samples for examination of the water soluble ion content has previously been carried out according to the standard DIN 38 414 (S4) elaborated for examination of water, waste water and sludge materials. Due to the standards application area, series of experiments were carried out in the present work to

test the standards applicability on bricks. Use of the standard resulted in satisfying accuracy, robust measurements and was subsequently used for the present investigations.

The total content of soluble ions verified both by the electrical conductivity measurements and as a sum of the actual anion and cation measurements clarified significant variations between bright, medium and dark colored new bricks (the color difference is shown in figure 1). Also significant differences in contents of soluble ions were found related to red/yellow color, location and age.

Resistance against acid was only found in a yellow brick whereas alkali resistance was absent both for red and yellow bricks.

The pH of a variety of bricks showed major differences related to exposure and a lower pH was shown in the bricks that had been a part of masonry for many years compared to new bricks.



Figure 1. Dark, medium and bright colored bricks.

The interaction between the pores and the overall pore system was studied to predict the electromigration in different bricks and the variations.

The pore structure and pore system in bricks are influenced by the firing degree, clay mixture composition and ion content. The pore structure and the pore system were investigated by neglecting other effects (clay mixture composition and ion content) by using the same brick type, produced at the same tilework and delivered at the same pallet. The bricks used were fired in a circular kiln, where uneven heating during firing occurs. Significant color differences were visible between the bricks in the pallet. For this investigation they were divided into the groups: bright, medium and dark colored bricks. The increasing color intensity was shown most likely to be caused by increasing firing temperature.

Saturation coefficient, open porosity, dry density and capillarity were measured for the three groups of bricks. Differences were seen. The pore system was studied in thin sections and showed by increasing brick firing temperatures a change from relatively many thin pores to fewer thicker pores. Also significant differences in the pore system as a function of distance to the surface were found.

Influence of the pore structure on the ion transport through the pore system of the bricks was made probable by electrical resistance measurements. An increasing resistance was found for increasing brick firing temperatures. The effective diffusion coefficient was empirically determined for chloride and sodium by application of an electric DC field across the bricks. The lowest effective diffusion coefficient was found for the dark colored brick, increasing for the medium and bright colored respectively. This suggests that in clay bricks many small pores favor ion transport in relation to fewer thicker pores.

Description of fundamental electrokinetics in bricks

According to the electrokinetic theory desalination through electromigration should occur first and then subsequently when low ion content in the pores are reached, drying through electroosmosis starts.

The effect of an applied potential gradient was investigated in laboratory experiments, with a red brick of the type Falkenløwe and an initial concentration of 1.0 wt% chloride,

added as sodium chloride. Successful desalination was obtained. At very low chloride and sodium contents in the electrolyte electroosmotic dewatering started. A second experimental series was made with focus on the change between desalination and dewatering, to estimate the ion concentration at which the change from electromigration as primary transport mechanism to electroosmosis as primary transport mechanism occurred. A transition from desalination as the primary phenomena to dewatering was shown when the average chloride content was reduced to around 0.01 wt% and therefore was this concentration termed the “point of starting dewatering”. On basis of measured surface properties (Cation Exchange Capacity) for different brick types, comparison with observations in laboratory scale for another brick type and observations from a previous pilot experiment the “point of starting dewatering” of 0.01 wt% chloride was found likely to be general valid.

Optimization of electrochemical salt removal from bricks

A laboratory setup approximated to real conditions and with ion contents corresponding to normal heavily polluted church vaults (1.0 wt% chloride, added as NaCl). A constant current of 40 mA was applied to the brick until the resistivity increased significantly or until satisfying desalination was obtained.

During the electromigration process acid and base were produced at the electrodes due to electrode reactions. If no precautions are taken the produced acid and base change the pH in the brick, leading to increased ion dissolution (weathering) and result in decreased electromigration efficiency of the contaminating ions out of the brick. In experiments where no precautions were taken, the extent of pH changes was shown significant and the acid (H^+) and base (OH^-) produced during the electrode reactions and resulted in non satisfyingly high desalination. New electrode units were developed to reduce these pH changes in the brick during the treatment. They consisted of metal net, kaolin clay and buffer components which were able to neutralize the produced acid and base. The results showed good ability to retain neutral pH values in the brick. Also the desalination process continued until a harmless salt content well below the Austrian ÖNORM 3355-1 threshold value was reached with the new electrode units.

Electromigration in pilot scale

Electromigration in pilot scale was tested on a NaCl contaminated wall section with murals. The wall section with murals is shown in figure 2. An applied current of 2.9 mA/cm was used, and the duration of the treatment was two weeks. Both chloride reduction in the wall section and accumulation of the extracted chloride in a removable poultice between the wall section and the electrodes were shown. The removal efficiency was high in some parts of the wall but low in other parts, dependent on how difficult it was to add distilled water to obtain a higher water content in the wall section. The higher water content the higher efficiency.

The pH was measured in the wall section before and after treatment and no changes were observed. Pigments in murals have very low solubility at neutral pH, but some pigments have increased solubility in extreme acidic or alkali environments. Since only



Figure 2. The wall section with murals. Height:88 cm, width:114.

dissolved pigments can be transported in an electric field, no changes in the pigments were expected after the treatment was ended, as the pH did not change after the electrokinetic treatment. Unfortunately, crumbling of the mortar below the cathode unit was observed during the treatment and further developments in the poultice type were needed.

A new cathode unit was developed consisting of a layered poultice. It was tested in acid-diffusion experiments regarding its ability to (a) hinder acid diffusion into the masonry, (b) its ability to remain a coherent system and (c) ensure good electric contact. These tests were made with layered poultices in plastic tubes which were placed on the masonry. The pH changes throughout the experiment were followed with acid-base color indicator in the multilayered poultice. The tested cathode unit consisted of: electrode, kaolin clay, buffer components in two layers and with or without a neutral poultice layer and with or without paper between the layers.

A three layered poultice with paper between the layers showed the best results. At the bottom of the cathode unit (which is to be placed on the masonry) pH was 7.6 and this must be considered as unproblematic. An electrode unit with the layered poultice was placed at a wall section for 11 days and the mortar stayed intact. The new cathode unit seemed satisfying; however, final approval must be carried out in tests with an applied electric field.

Examination of the salt deterioration cause in praxis

Since the salt deteriorating effect is dependent of the actual present ions, mixtures and climate the deterioration process was studied on a location with extensive salt induced surface deterioration and maybe an object of future desalination. The location was a salt contaminated vault of the so-called Birdsroom in the Carmelite Monastery (Vor Frue Monastery) in Helsingør, Denmark. A picture of the vaults is shown in figure 3. The investigation was carried out by use of Scanning Electron Microscopy (SEM) - Energy Dispersive X-ray Spectroscopy (EDX) analysis.



Figure 3. The vaults of the Birdsroom in the Carmelite Monastery, Helsingør, Denmark.

Samples were taken from the masonry at the loft above the vault, at the upper surface of the vault itself and from repealed materials below the vault.

The investigations showed that the primary salt contaminant was sodium chloride used for preservation of perishable food in ancient preservation. Meanwhile, the most accepted theory for salt deterioration, crystallization pressure, does not justify damage from sodium chloride alone.

Besides sodium chloride, sulfur was found at all fractures originating from the vault by element mapping with (EDX) mappings. Overlapping EDX mappings with calcium, oxygen and sulfur made probable that gypsum was the determining deterioration factor. These SEM-EDX analyses underline the importance of individual evaluation of damaging ion concentrations related to the actual salt mixture since the study showed that the highest ion concentration not necessarily is the causes for the damage and since the combination of salts can result in another degree of damage than in the case for the single salts themselves. This has to be taken into account in future desalination treatments of existing structures for determination of a satisfying ion reduction will be obtained.

Resume

På nuværende tidspunkt er der mangel på effektive metoder til saltudtrækning af murstenshvælv med kalkmalerier. Salte kan forårsage overflade nedbrydning og dermed ødelæggelse af kalkmalerier. I de tilfælde hvor salt forårsager nedbrydning af kalkmalerier i små områder, kan de genmales og det visuelle indtryk dermed bevares i yderligere en årrække. Da kilden til nedbrydningen imidlertid ikke er fjernet vil den kostbare nedbrydnings-genmalings cyklus fortsætte. Ved omfattende nedbrydning af store områder er genmaling ikke altid en mulighed.

Nærværende afhandling er baseret på en hypotese om, at bruge de elektrokinetiske fænomener til at accelerere og opnå en effektiv afsaltnings af murstensmurværk over kalkmalerier til bevaring af kalkmalerier. Et fænomen som tidligere har vist sin effekt i finkornede og porøse materialer.

Nærværende afhandling har til formål, at dokumentere den elektrokinetiske afsaltnings effekt, identificere bivirkningerne og optimere processen i murstensmurværk i forbindelse med malede overflader (kalkmalerier).

Undersøgelserne var opdelt i:

- Karakterisering af mursten
- Beskrivelse af fundamental elektrokinetik i mursten
- Optimering og udvikling af metode
- Elektromigration i pilot skala
- Undersøgelse af salt nedbrydning i praksis

Karakterisering af mursten

Murstens karakterisering blev udført både mht. mængden af opløselige ioner og pH-værdier i relation til miljømæssige påvirkninger og brændingstemperaturens indflydelse på murstens poresystem. Denne opdeling havde til formål at adskille ionindholdet og poresystemets indflydelse på den elektrokinetiske transport.

Murstensmurværk bliver påvirket af forskellige miljømæssige faktorer bl.a. syreregn. Miljømæssige faktors effekt på mursten blev undersøgt på et udvalg af mursten: nye og gamle (relateret til placering og påvirkning), røde og gule samt produktionsmåde (tunnelovn, ringovn). Effekten og omfanget af den miljømæssige påvirkning (fra fx syreregn) var målelig på både mængden af opløselige ioner og pH-værdien.

Forberedelsen til undersøgelse af det vandopløselige ion indhold i murstens- og klinkerprøve er tidligere blevet udført i henhold til standard DIN 38 414 (S4), udarbejdet til undersøgelse af vand, spildevand og slammaterialer. Pga. standardens anvendelsesområde, blev serier af eksperimenter udført for at teste anvendeligheden i

forbindelse med mursten. Brug af standarden resulterede i tilfredsstillende nøjagtige, robuste målinger og blev efterfølgende brugt til undersøgelserne.

Den totale mængde af opløselige ioner, blev målt både ved den elektriske ledningsevne og som en sum af de aktuelt målte anioner og kationer. Den tydeliggjorde signifikante forskelle mellem lyse, medium og mørk farvede nye mursten (farve forskellene er vist i figur 1). Der blev også fundet signifikante forskelle mellem indholdet af opløselige ioner relateret til rød/gul farven, placering og alder.



Figur 1. Mørk, mellem og lys farvede sten.

En vis evne til at modstå ændringer i pH-værdien ved syrepåvirkning blev kun fundet i en gul

mursten. Modsat var der ikke var nogen målelig evne til at modstå pH ændringer ved basepåvirkning for hverken røde eller gule mursten.

Der blev målt en signifikant forskel i pH-værdien for et udvalg af mursten relateret til påvirkning, og der blev målt en lavere pH værdi for mursten, som havde været en del af et murværk i mange år sammenlignet med nye mursten.

Sammenhængen mellem de enkelte porer og det overordnede poresystem blev undersøgt for at kunne forudsige elektromigrationseffekten i forskellige mursten og variationen mellem murstenene.

Porestrukturen og poresystemet i mursten er afhængig af brændingsgrad, sammensætningen af lerblandingen og ionindhold. Porestrukturen og poresystemet blev undersøgt ved at negligere andre effekter (lerblandingssammensætning og ionindhold) ved at anvende den samme murstentype, fremstillet ved det samme teglværk og leveret på den samme palle. De anvendte mursten var brændt i en ringovn, hvor der forekommer inhomogen varme under brændingen. Der var betydelig farveforskel på murstenene fra den samme palle. Til undersøgelsen blev de inddelt i farvegrupperne: lys, mellem og mørk. Det blev vist, at den forøgede farveintensitet højst sandsynligt skyldes en højere brændingstemperaturer.

Den kapillære vandmætningsgrad, den åbne porøsitet, tørdensiteten og kapillaritetstallet blev målt for hver af de tre grupper mursten. Forskelle blev målt mellem de tre grupper mursten. Poresystemet blev undersøgt vha. tyndslib og viste ved stigende murstensbrændingstemperaturer en ændring fra relativt mange tynde porer for en lys mursten til færre tykkere porer for en mørk mursten. Der blev også målt signifikante forskelle i poresystemet, som en funktion af afstanden til overfladen. Der var relativt større porer ved overfladen end ind mod midten.

Porestrukturens indflydelse på iontransporten gennem murstenens poresystem blev sandsynliggjort ved måling af den elektriske modstand. Der blev målt en højere elektrisk modstand ved stigende brændingstemperaturer for murstenene, dvs. højest modstand for den mørke mursten. Den effektive diffusionskoefficient blev empirisk bestemt for klorid og natrium ved at påtrykke et elektrisk felt over en mursten. Den laveste effektive diffusionskoefficient blev beregnet for den mørke mursten, stigende for henholdsvis den medium og lyse farvede mursten. Dette sandsynliggør, at mange små porer begünstiger iontransporten i forhold til færre store porer i lermursten.

Beskrivelse af fundamental elektrokinetik i mursten

Ifølge den elektrokinetiske teori, vil afsaltning ved elektromigration ske ved høje ionkoncentrationer. Ved lave ionkoncentrationer vil der ske elektroosmotisk udtørring. Effekten af et påtrykt elektrisk jævnstrømsfelt blev undersøgt i laboratorieforsøg, med en rød mursten produceret af Falkenløwe og med en begyndelseskoncentration på 1,0 vægt% klorid, tilsat som natriumklorid. Succesfuld afsaltning blev opnået. Ved meget lave koncentrationer af klorid og natrium koncentrationer startede den elektroosmotiske afvanding.

En anden eksperimentel serie blev ludført med fokus på ændringen mellem afsaltning og udtørring. Formålet var at estimere den ionkoncentration, hvor der sker en ændring fra elektromigration til elektroosmose som den primære transportmekanisme. Det blev vist, at overgangen fra afsaltning til afvanding som primært fænomen skete, når det gennemsnitlige kloridindhold blev reduceret til ca. 0,01 vægt%. Derfor blev denne koncentration kaldt ”punktet for begyndende afvanding”.

På baggrund af de målte overfladeegenskaber (kation ombytter kapaciteten) for forskellige murstenstyper, sammenlignet med observationer: under laboratorieforsøg med andre murstenstyper samt et tidligere pilotforsøg blev det sandsynliggjort, at ”punktet for begyndende afvanding” er generelt gyldigt.

Optimering af elektrokinetisk saltfjernelse fra mursten

Der blev designet en laboratorieopstilling, som blev tilnærmet eksisterende forhold og med ionindhold svarende til normal, høj saltbelastning i kirkehvælv (1,0 vægt% klorid, tilsat som NaCl). En konstant jævnstrøm på 40 mA blev påtrykt over murstenene indtil modstanden steg signifikant, eller indtil tilfredsstillende afsaltning var opnået. Elektrodeprocesser er en elementær del af det elektriske kredsløb og forårsager som en del af elektromigrationsprocessens syre- og basedannelse ved elektroderne. Såfremt der ikke tages forholdsregler overfor den dannede syre og base, vil der ske ændringer i murstens pH værdi, hvilket resulterer i forøget opløselighed af ioner (forvitring) og i en formindsket elektromigrationstransport af de bygningskadelige ioner ud af murstenen. I de forsøg hvor der ikke blev taget forholdsregler overfor den dannede syre og base, var pH-ændringerne ganske betydelige. Den producerede syre (H^+) og base (OH^-) forhindrede en tilfredsstillende afsaltningseffekt. Nye elektrodeenheder blev udviklet til at reducere disse pH-ændringer i murstenen under afsaltningen. De nye elektrodeenheder bestod af: metalnet, kaolin ler og buffer komponenter, som gjorde det muligt at neutralisere den producerede syre og base. Resultaterne viste, at de nye elektrodeenheder havde en god evne til at bibeholde neutrale pHværdier i mursten. Ved anvendelse af de nye elektrodeenheder var det muligt at fortsatte afsaltningsprocessen kontinuert indtil der var opnået et uproblematisk saltindhold betydeligt under den østrigske norm 3355-1's grænseværdi.

Elektromigration i pilot skala

Elektromigration i pilot skala blev afprøvet på et NaCl forurenset vægudsnit med kalkmaleri. Vægudsnittet med kalkmaleri er vist i figur 2. Der blev anvendt en konstant jævnstrøm på 2.9 mA/per cm elektrode, og behandlingen varede 2 uger. Resultaterne viste både en reduktion i vægudsnittets kloridindhold samt akkumulering af den udtrukkede klorid i det aftagelige offerlag som var placeret mellem væggen og elektroderne.

Saltudtrækningseffektiviteten var høj i nogle af væggenes områder, men lav i andre områder, afhængig af hvor nemt det var at opfugte de enkelte områder. Jo højere vandindhold i de enkelte områder, jo højere effektivitet.

Der blev målt pH-værdier for vægudsnittet både før og efter behandlingen. Der var ingen målelig ændring. Kalkmalerierspigmenter har en meget lav opløselighed ved neutral pH, men nogle pigmenters opløselighed forøges i ekstremt surt eller basisk miljø. Da udelukkende opløste pigmenter kan transporteres og da pH ikke ændrede sig under den elektrokemiske behandling i et elektrisk felt, blev der ikke forventet ændringer i pigmenterne. Der blev heller ikke observeret nogen pigmentændringer. Under behandlingen smuldrede mørtlen under katodeenheden og yderligere udvikling af katodeenheden var følgelig nødvendig.

Der blev udviklet en ny katodeenhed bestående af lagdelt offerlag. Dens evne til (a) forhindre syre diffusion ind i murværket (b) til at forblive et sammenhængende system samt (c) sikre god elektrisk kontakt blev testet i syre-diffusions forsøg. Disse tests blev udført i plastik rør, som blev placeret ovenpå murværket. pH ændringer blev fulgt under eksperimentet med syre-base farveindikator i flerlagsofferlaget. De testede katodeenheder bestod af: elektroder, kaolin ler, buffer komponenter, nogle med et neutralt lag og nogle med porøst papir mellem lagene.

Et tre-delt offerlag med porøst papir imellem viste de bedste resultater. I bunden af katodeenheden (som skal placeres på murværket) var pH 7.6, hvilket er uproblematisk. Elektrodeenhederne med det lagdelte offerlag blev placeret på murværket i 11 dage, og mørtlen forblev intakt. De nye katodeenheder virkede tilfredsstillende; men endelig afprøvning må ske i tests med et påtrykt elektrisk felt.



Figur 2. Væg udsnittet med kalkmaleri. Højde: 88 cm, bredde: 114 cm.

Undersøgelse af saltnedbrydningsårsager i praksis

Saltnedbrydning er afhængig af de aktuelt tilstedeværende ioner, blandinger og klima. Derfor blev nedbrydningsprocessen undersøgt på et sted, hvor den saltforårsagede overfladenedbrydning var omfattende. Stedet var et saltforurenset hvælv i det såkaldte Fugleværelse i Karmeliter klosteret (Vor Frue kloster) i Helsingør, Danmark. Et billede af hvælvene er

vist i figur 3. Undersøgelserne blev udført ved brug af et Scanning Electron Microscopy (SEM) -



Figur 3. Hvælvene i Karmeliter klostrets Fugleværelset, Helsingør, Danmark.

Energy Dispersive X-ray Spectroscopy (EDX) analyser.

Der blev udtaget prøver fra klosterets loft ovenover hvælvet, på selve hvælvets overflade og fra nedfaldet materiale under hvælvet.

Undersøgelserne viste, at den primære årsag til saltforureningen var natriumklorid, som sandsynligvis tidligere blev brugt til konservering af fordærveligt mad. Imidlertid retfærdiggør den mest accepterede saltnedbrydningsteori, krystallisationstryk, ikke for skader alene forårsaget af natriumklorid. Udover natriumklorid, blev der også fundet sulfur i brudfladen, på alle de nedfaldne kalklag stammende fra hvælvet (vha. EDX element mapping). Overlappende EDX mappings med calcium, oxygen og sulfur sandsynliggjorde, at tilstedeværelse af gips var den afgørende nedbrydningsfaktor.

Studiet viste, at den højeste ionkoncentration ikke nødvendigvis er den primære skadesårsag og understreger derfor at en individuel evaluering af de skadelige ionkoncentrationer i relation til de aktuelle saltblandinger er nødvendig. Ydermere kan den aktuelle saltkombination resultere i et andet skadesomfang end for de enkelte salte hver for sig. Disse overvejelser bør medtages ved kommende afsaltningsbehandlinger på eksisterende konstruktioner til vurdering af, hvornår der er opnået en tilfredsstillende reduktion af ionindholdet.

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Structure of the thesis

The aim of the present PhD study was to investigate the possibility of electrokinetic extraction of the damaging salts from brick masonry vaults for preservation of murals. However, since only little documentation was available before the study was started, the documentation was ongoing in steps to minimize misinterpretations and indeed not all the steps towards final approval were carried out during the study.

In the first 3 background sections, the intension was to introduce the reader to the three areas: murals (chapter 1), salts (chapter 2) and electrokinetics (chapter 3). These three chapters should prepare the reader to new application areas since collaboration between electrokinetic and building materials is untraditional and thereby to ease the reading of the following six papers. Specific effects, parameters etc are not included in the introducing chapters but is extensive described in the following papers.

The six papers are divided into the areas: characterization of bricks (paper I-II), fundamental electrokinetic in bricks (paper III), developments for electrokinetic desalination (paper IV), electromigration in pilot scale (paper V) and salt deterioration in praxis (paper VI). The first four papers (I-IV) deals with single bricks, the fifth paper (V) with a brick masonry wall section with murals and the sixth (VI) likely salts deteriorating in a case study of a painted vault in Helsingør Denmark.

The characterization section consists of:

The first paper: “The environmental effect and the colors influence on soluble ions in bricks” is a chemical characterization of the water soluble ion content, measured both by the electrical conductivity and as a sum of the actual anion and cation measurements. A significant difference of the water soluble ion content was found for a variety of red/yellow color bricks dependent of location and age. Coherence between pH in bricks related to age, position and color was also found.

The following paper “Diffusion and electromigration in clay bricks – influenced of the firing induced differences in the pore system” describes macroscopic variations mainly between poorly and hard fired bricks through thin sections, saturation coefficient, open porosity, dry density and water absorption coefficient. The pore structures impede on the ion transport through the brick was measured as the total resistance in a brick, the effective diffusion coefficients for sodium and chloride in bricks was also measured and a consistency between the parameters found.

The fundamental electrokinetic section

Consists of the third paper “Electromigration versus electroosmosis in a clay brick under non steady laboratory conditions” describes the ion concentration at which the primary electrokinetic effect change from electromigration to electroosmosis in clay bricks and an applied electric DC field. The ion concentration at which the primary electrokinetic effect change is termed “the point of starting dewatering”. This “point of starting dewatering” was through measurements of material properties and observations from both laboratory scale and pilot scale made probable to be general valid.

The development section

Consists of paper IV “Development of a poultice for electrochemical removal from bricks – Effects and side effects” and clarifies through the chosen setup as an example, the extend of produced acid and base during the electrokinetic desalination as a consequence of the electrode reactions. In the paper it is shown that there is a need for hindering the produced acid and base to enter the substrate (here brick). Therefore a poultice was developed which made it possible to obtain a high desalination effect and maintain a neutral pH.

Electromigration in pilot scale

Is described in paper V: “Desalination of a wall section with murals by electromigration” where the electrokinetic desalination effect was tested in pilot scale and possible pH changes measured with satisfying result. However, during the investigation mortar crumbling was observed below the cathode unit and further improvements were needed. These additional developments are described in Appendix 1 “Further development of poultice for electrochemical removal from bricks”.

Salt deterioration in praxis

Is treated in the last paper “Impact of gypsum formation on deteriorating of a painted monastery vault shown by SEM-EDX analysis” is a case study of the deterioration in the bird’s room at the Carmelite monastery in Helsingør, Denmark. This paper is a contribution to the understanding of the salt deterioration mechanism which has been studied for more than hundred years but still is not fully understood. Sampling from the deteriorated murals and the surrounding, analyzes by SEM-EDX (mainly from the fractures) made it probable that the presence of sodium chloride accelerated the gypsum formation through repeating dissolution-crystallization cycles and caused the extensive deterioration.

During the work with the papers I-VI, additional correlations and new questions appeared and they are described in chapter 4: Discussion of perspectives and future work, among these are: the effect of varying water contents on the electrokinetic effect and electroosmotic dewatering followed through the resistance measurements. Finally, the overall conclusions are outlined in chapter 5.

1. Murals: history, salt deterioration and precautions

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Introduction

Salt induced deterioration of murals and cultural heritage in general receive increasing attention in Denmark. It has been recognized that treatment is necessary to avoid loss of invaluable heritage.

Generally, maintenance of buildings is necessary to avoid extensive damage, and thereby save costs in the long term and increase the comfort. However, in connection to heritage, maintenance is essential to prevent the old buildings from fall into decay. Especially for heritage buildings a minimum of interference is demanded and destructive interference should be avoided.

In Denmark there are around 9000 heritage buildings and around 300.000 buildings worth preservation [Kulturarvsstyrelsen]. For these buildings it is of highest importance to ensure that applied salt extraction methods not are connected with adverse effects and extensive documentation is necessary before use.

At present there is a lack of effective salt extraction methods from murals and in case of deterioration the murals are repainted. However, as the source for the deterioration salts is still present in the brick masonry vault and lime layer with the murals, the deterioration-repainting cycle is unfortunately continuing, figure 1. In case of extensive deterioration of larger areas, repainting might be impossible.

As the traditional building material in Denmark for old buildings worth preservation is often bricks and as most church vaults are constructed from bricks, brick is the main material which is investigated in the present work. Furthermore, in the rest of Northern and Middle Europe, heritage buildings are almost exclusively made from brick masonry including most churches and their vaults. Thus the work may be useful not only for preservation of murals in Danish churches, but also internationally.

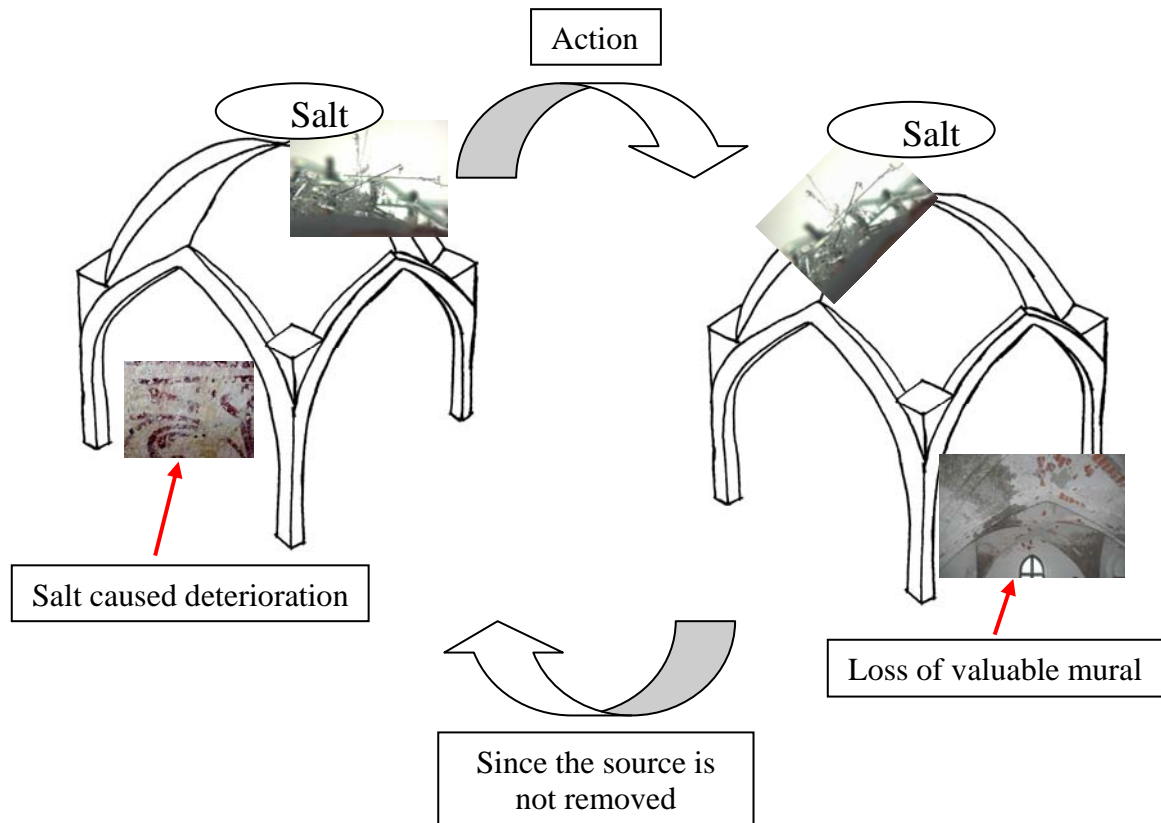


Figure 1. Present salt induced deterioration of murals. The salts are present in the brick masonry vault and in the lime layer and results in repulsion of small areas with paint. The murals are repainted when possible. However, since the source for the deterioration is not removed the deterioration-repainting cycle unfortunately continuous.

1.1 Danish murals and church vaults in a historic perspective

1.1.1 Introduction to the Christianity

The Danes were introduced to the Christianity after Harald Bluetooth was baptized around 940 after Christ. He was probably baptized to get the German empire as friend and allied. As a consequence of the King's baptism the Danes were forced to be Christians, too. The Christianization of the Danes was demanded within a relatively short period, even though it was a huge change to be Christen. The Christianity is very different from the old Nordic Mythology, which was practiced at that time. Painting the vaults with murals, with religious stories were used to introduce the new religion and to hand on the Christian stories in picture language [Nørregård-Nielsen, 2003]. Until the reformation the spoken language during the service was Latin. As most Danes were neither able to read nor to understand the spoken Latin, the new Christian religion was solely introduced by picture language through the murals [Stilling, 2004]. Today, murals in the shape of picture languages from an ancient time, gives a seldom insight in the way of thinking at the time they were made. Furthermore, art from churches is almost the only art known from the early Danish time [Nørregård-Nielsen 2003]. All this makes the murals outstanding and indeed worth preserving.

1.1.2 Development in the type and amount of Danish churches

In the end of the 1000 centuries a history writer claims that there were 300 churches in Scania, 150 on Zealand and 100 on Funen. At this time the old connection to England affected the Danish churches and the first stone churches were erected with English inspiration or even by English master builders. The main part of the churches was made in wood at this time. Around 1150 the construction of stone churches was intensified. Around year 1250 AD only few wooden churches remained and instead around 2000 stone churches existed within the current borders of Denmark. After 1250 AD only few new churches were built as the need was covered. An exception was the expanding marked towns where churches after 1300 AD were built in gothic style. In the 14th century a new step of church constructions was initiated. This new step was again initiated by the nobility in order to make their churches more visible. In the second half of the 14th century: porch, side chapel and spires were built [Stilling, 2004]. The main parts of the Danish churches are built in mediaeval times in roman style. Within the current borders of Denmark are around 1700 medieval churches and from these are around 700-800 churches built after 1850 AD [Stilling, 2004].

1.1.3 Murals

After 1350 AD (gothic time) the flat roof ceilings were often replaced with masonry vaults and by whitewashing these vaults the base for the murals was created [Stilling, 2004]. Accordingly murals were painted even in the smallest and poorest churches with the artist's bible stories. In this period the murals were painted simple. Yellow and red were used as basic colors. However, some of the Danish village churches are very distinguished and sometimes valuable decorated (famous artist and/or with expensive pigments). These paintings are assumed to be paid and perhaps also decided of the squires, who had traveled in foreign countries and were inspired there.

The colors in the murals tell their own stories. E.g. the enamel blue ultramarine color was manufactured from crushed lapis from Persian and the Spanish green color was fetched from Sicilian or Spain. The import of the pigments from such far-off countries made them very valuable. Contrary, soil colors including colors from red to brown to ochre and yellow were cheap to manufacture from materials present in Denmark. An example of a valuable decorated church is Kirkerup Church, Zealand, Denmark (figure 2), which through the use of the blue color and gold showed the church's wealthiness. Kirkerup Church's wealthiness is ascribed its connection to Roskilde cathedral in ancient time.

The murals motives are from the Testament the New and Old and represent a public version of the bible. Often the murals have upbringing and frightening pictures. Good,



Figure 2. Original, but refreshed mural from Kirkerup church (around 1200 AD).

Maria, the crucified Christ and different saints are the leading character in the murals [Stilling, 2004].

These circumstances make the murals to unique Danish Cultural heritage and besides the murals extraordinary importance to the Danish history they are also unique in an European context.

1.1.4 Covering and recovering of the murals

After several hundred years some murals seemed worn out and they were partly covered with a lime wash and partly knocked down. Incense and candlelight had been burned for centuries in the churches resulting in a film of fat, which covered the walls and vaults and protected the lime washed and painted surfaces [Nørregård-Nielsen, 2003]. The murals were still visible in the 1700 th. century in many churches. In the 1730's and 1740's were the pietism was generally accepted, the remaining medieval murals were covered with lime wash. This is in contrast to the myth, which claims that the murals were abolished and immediately covered in 1536 after the reformation [Stilling, 2004].

The first murals were recovered in Denmark by the pioneers J. Magnus Petersen and Jacob Kornerup in the second half of the 1800 th. century. The methods were hacking and reconstruction of the paintings. These rather radically actions were mainly due to the lack of methods we have today [Stilling, 2004].

The protection of the murals behind the films from incense and candlelight have made it possible to recover many of the original murals with still better methods in the last centuries [Nørregård-Nielsen, 2003]

1.2 Deterioration of the murals

Even though paintings on church vaults have existed for hundreds of years, an accelerated deterioration has been observed within the last hundreds of years and especially within the last decades by conservators from the Danish National Museum. The primary reason for this deterioration is salts. Especially high amounts of sodium chloride (NaCl) are present in some vaults. The accelerated deterioration is partly due to heating (which changes the relative humidity) and partly due to uncovering of the paintings which resulted in changed evaporation zones in the structures [Larsen, 1999].

Dependent on temperature and relative humidity of the surrounding climate, salts as NaCl is either precipitated as salt crystals or present as ions in the pore solution. According to the most accepted theory the phase change from solute ions to precipitated salt crystals is the primary cause for deterioration of the murals. The deterioration occurs in small areas where the lime layer is pushed of, figure 3.

As Danish village churches are only heated for services, the relative humidity inside the church vary significant within on week during the winter. The combination of



Figure 3. Close up of a partly deteriorated mural. Rørby Church, Denmark

significant changes in the relative humidity and salts in the vaults, a dissolution-nucleation cycle occurs just within one week in the winter period and results in an accelerated deterioration.

Murals in Danish churches are continuously maintained. Traditional maintenance consists of dirt cleaning from the murals surfaces and is carried out approximately every 50 year. In case of salts in the bricks (also termed sick bricks) in the vault restorations must be expected at least every 10-20 years, according to conservators. Repainting of murals is expensive and since most Danish churches are owned from the local parish a traditional restoration can be non manageable financially. However, if restoration isn't carried out before it is too late; the consequence is loss of the valuable murals, of which figure 4 is an example.

The state of 330 murals in Danish churches was examined [www Trampedach, 2008] and from these 33 had salt problems.



Figure 4. Deterioration of the murals in the Carmelite Monastery in Helsingør, Denmark.

1.3 Salt extraction methods

Presence of salts is not only a problem in church vaults. Also other constructions may suffer from salt induced decay e.g. plastered buildings. The salts cause damage for enormous amounts. Several projects were recently finished and some are still ongoing by researchers, primarily from Europe.

An EU project dealing with a method to limit salt damage by use of inhibitors was finished in 2007 (section 1.3.1), an EU project dealing with use of compress plaster for salt extraction is ongoing (section 1.3.2), previously use of climate chambers for accelerated ion transport was investigated in Denmark (1.3.3) and the present thesis deals with electrokinetic desalination (section 1.3.4). International salt conferences are organized e.g. “Salt Weathering on Buildings and Stone Sculptures, Copenhagen, Denmark 2008”, “Salt Damage Congress, Ghent, Belgium 2007”, “Mauersalze und Architekturoberflächen, Dresden, Germany 2002”, which shows an interest internationally for salt deterioration within the last years.

1.3.1 Inhibitors

Inhibitors are believed to act in two principal ways: (a) as crystallization inhibitors, preventing or delaying the formation of stable nuclei, although in some instances additives can act as nucleation promoters; and (b) as habit modifiers, through adsorption onto specific faces of a growing crystal, thus decreasing (or increasing) their growth rates.

The tool to obtain this is addition of different chemicals as e.g. ferrocyanide [Rodriguez-Navarro et al., 2002]. This means that the damaging salts are not removed;

but aimed to transform the salts inborn damaging action to non-damaging. The project included also investigation of how the salt crystals are formed [www EU project SALTCONTROL].

1.3.2 Compress plaster

A compress plaster is a removable layer which is used for accumulation of damaging ions. By use of compress plaster the ions are transported due to concentration differences, as a part of evaporation (drying) at the surfaces or due to capillary differences between the compress plaster and the underlying substrate. In all cases the ions are indirectly affected. Traditional poultice can consist of one or more of the following components: cellulose, clay (bentonit, kaolin), newspaper, sand, filler etc. Compress plasters have been used for salt extraction from structures for several years and is described in WTA- technical bulletin E-3-13-01/D [WTA, 2001]

The design of a traditional compress plaster is made on basis of several factors: ensure a good contact between the substrate and the compress layer, control of the evaporation degree in the compress layer to ensure that the evaporation zone is in the compress layer and not in the original salt contaminated material. This means that a number of material characteristics must be optimized such as: Damp diffusion resistance, capillary number, porosity [Pauner et al., 1999]. The compress plaster should be relatively more fine porous than the underlying material to obtain the evaporation zone in the compress plaster. Therefore is the optimal compress layer dependent of the specific construction. The method is at present investigated in a project [www EU project DESALINATION] with the aim, to give recommendations of the optimal compress plaster for different material.

This indirect affect by use of compress plaster is difficult to control and is dependent of several factors and the compress plaster should be controlled every week [Grassegger-Schön, 2002].

1.3.3 Climate champers

When installing climate champers inside a church it is possible to establish controlled climates. The damaging crystallization-dissolution cycle of the salts can then be stopped by choosing a relative humidity either below or above the crystallization point of the actual salts [Larsen, 1999].

Dissolved salts (ions) are transported together with the liquid during drying towards the evaporation zone, where the surface at which drying occurs is dependent of the seasonal changes. By use of climate champers in combination with compress plaster, the aim is to increase the salt extraction velocity and effectively by controlling where the drying zone comes into existence. Establishment of a moist climate at one side of a construction and a dry climate on the other side of the construction can result in an accelerated evaporation (meaning water and ion transport) towards the driest climate. A combination of compress layer and climate control creates the possibility to remove the salts after ended treatment [Larsen, 1999]. Also this transport of the ions is indirect and is in practice difficult to control. Larsen (1999) documented a reduction to 0.2 wt%

cation content (sodium) in a pilot scale test which seemed to be the lower obtainable value in praxis for the desalination of bricks using this method. This value is caused by a decreasing diffusion induced ion transport until the effect at some point is neglectable [Larsen, 1999].

1.3.4 Electrochemistry

By application of an electric DC field, dissolved salts (ions) are affected directly and a controlled transport can be obtained.

Preservation of Buildings (e.g. dwellings and churches) with electrokinetics has been offered for around 30 years in some countries in Europe (e.g. Germany, Austria, Switzerland, Norway). Nevertheless the method was until recently not accepted by independent research institutes neither in Denmark nor in several other countries.

However, since 2007 is the electrokinetic effect in brick masonry described as proven in laboratory scale in a technical guide by [GI, 2007].

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2. Salt distribution, deteriorating mechanisms and damaging concentrations

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Introduction

Presence of salts in existing structures is unfortunately a well known problem. The salts can appear as undamaging effluences at the surface (figure 1 (a)), or appears as damaging subeffluences (figure 1(b)). In case of plastered walls, the plaster can peel of in a belt (figure 2 (a)) or in some specific areas (figure 2 (b)) dependent of the source for the salt contamination. Salts in combination with rising dampness results in plaster peeling in a belt whereas salt contaminated single bricks (e.g. originating from salt contamination during manufacturing) results in plaster peeling in front of these. The analogousness between these four cases is that the salts are undesired and results in increased costs and maintenens.



Figure 1. (a) Harmless salt effluences at the surface of non plastered brick masonry from where the salts can be removed by use of a brush. (b) Material damaging subeffluences (salt crystallization inside the pores).



Figure 2. Plaster peeling (a) Traditional salt induced plaster peeling in a belt at approximately the same distance from the ground (b) Peeling of the lime wash in front of some specific bricks. In both cases the result is increased maintenance.

Salt induced plaster peeling in connection with Cultural Heritage has the additional aspect, that deterioration result in loss of invaluable original material (figure 3). The deterioration process is the same as in case of plaster peeling from traditional structures.



Figure 3. Salt induced deterioration of murals (a) From a monastery vault (b) From a church vault.

Due to the huge impact of salt induced damage on increased maintains, increased costs and loss of invaluable Cultural Heritage, salt related deterioration and tests have been known for centuries. However, the salt induced deterioration is still an unsolved problem and new investigations are still conducted. Several salt research projects have been carried out both in relation to traditional buildings and e.g. in 2007 a special Journal issue was published [Environ Geol, 2007] and in relation to painted vaults: “Konservierung von Wandmalerei” [Pursche, 2001] “Forschungsproject Wandmalerei-Schäden” [Segers-Glocke, 1994], “Salzschäden an Wandmalereien” [Bayerischen Landesamtes für Denkmalpflege, 1988].

In the following an introduction to salts distribution (section 2.1), deteriorating mechanism (section 2.2) and threshold values (section 2.3) are given.

1. Salt distribution in masonry

When the source for the salt contamination is searched, knowledge of general salt distribution is necessary. The salt distribution can be divided into:

- The horizontal crystallization zone (distance from the surface) and the influence from the material
- The vertical crystallization zone (distance from the ground) and the influence from the specific ions solubility's

1.1 The horizontal crystallization zone

The actual salt distribution is dependent on the material properties (porosity, poresize distribution ect.) and the surrounding climate (temperature and relative humidity), however the tendency for salt accumulation at the surface or just below the surface of the structures in dry climate is similar for all materials. Auras & Melisa (2002) suggested the typical salt profile shown in figure 4.

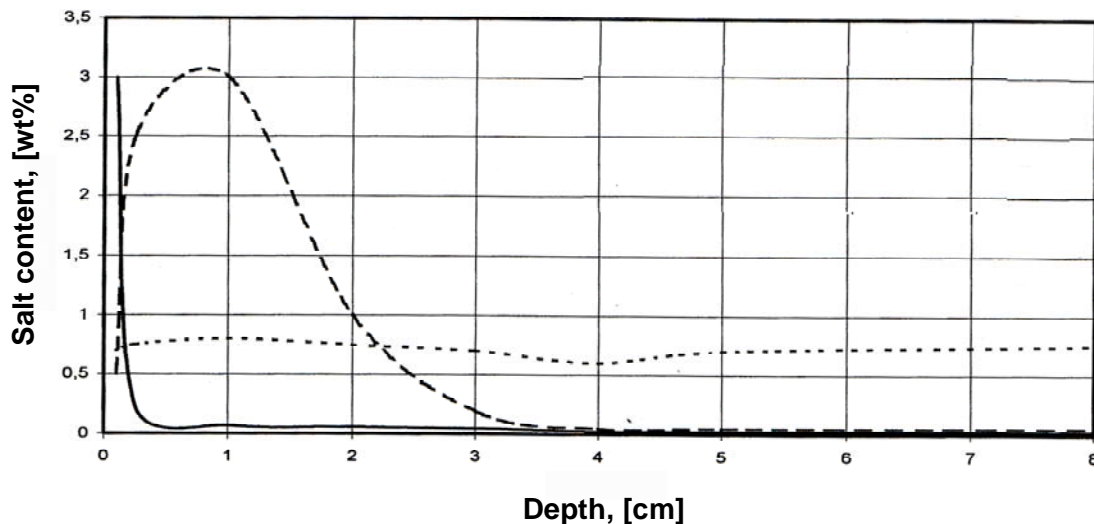


Figure 4. Typical salt distribution in an external wall from [Auras & Melisa, 2002]. The solid line represents salt-crust at the surface, the big dotted line salt accumulation near the surface and the small dotted line the salt contamination of the cross section.

Salt crystallization occurs in the structure at equilibrium between evaporation (the moisture transition coefficient of the surface) and liquid transport towards the surfaces (the moisture transport coefficient) [Snethlage & Wendler, 1997], [Lewin, 1978], [Lubelli et al., 2006b]. The distance of salt precipitations from the surface is mainly dependent of the pore size distribution and the relative humidity of the surrounding climate. The smallest fraction of the pores causes' capillary suction, is thereby the driving underpressure and the reason for the water uptake. The pore fraction with the largest diameters contributes to the evaporation. Therefore the exact combination of small and big pores (termed poresize distribution) decides the materials influence on the evaporation mechanism [Frössel, 2002].

Snethlage & Wendler,(1997) calculated by a numerical model by Künzler (1994) the depth of this evaporation zone from the surface in depth for different natural stones with varying density. Coherence for the depth of evaporation was found between increasing

density and in depth reduced evaporation zone and between evaporation zone and the detachment zone through experiments with a test wall. Rodriguez-Navarro & Doehne (1999) suggested differences in crystallization patterns between reduced deterioration in case of crystallization at the surface (for NaCl) and extensive deterioration by crystallization inside the pores (for $\text{NaSO}_4 \cdot 10\text{H}_2\text{O}/\text{Na}_2\text{SO}_4$) on basis of laboratory experiments.

Pel et al. (2003) showed with Nuclear Magnetic Resonance (NMR) measurement in NaCl contaminated fired clay bricks, that the initial primary mechanism during drying is advection. The result is relative high salt concentrations at the surface compared to the inner parts of the material. When the drying out becomes more advanced diffusion becomes dominating and the ion profiles more uniform [Pel et al., 2003].

In summery does the damaging salt crystallization occurs close to the surface in a layer where the water supply velocity from the construction is lower than the evaporation velocity. However, the distance of the evaporation zone and thereby the salt crystallization zone from the surface is dependent of the actual pore size distribution in the material.

1.2 The vertical crystallization zone

Arnold & Zehnder (1987) found by numerous observations, documentation and analysis of existing structures a link between the precipitation height of the anions above the ground and the solubility product of the salts. In table 1 it is seen that sulfate salts in general have lower solubility than nitrates and chlorides, however, addicted of the actual formed salt. The least soluble sulfate precipitates in a relative smaller distance from the ground than the more soluble nitrates and chlorides, figure 5. However, in case of salt mixtures deliquesce humidity can be significantly changed. E.g. the influence on the solubility of gypsum from other soluble salts e.g. NaCl was outlined by Lubelli et al. (2004) based on Price & Brimblecombe (1994) and experimentally shown to increase the solubility of gypsum with up to a factor three in combination with NaCl [Charola et al., 2007].

Table 1. Solubility products related to the anions sulfate, nitrate and chloride.

| | SO_4^{2-} [g/L] | NO_3^- [g/L] | Cl^- [g/L] |
|------|--|------------------------------------|-------------------------|
| Ca* | 2.2 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | 3760 $\text{Ca}(\text{NO}_3)_2$ | 1590 CaCl_2 |
| Na** | 162 Na_2SO_4 | 880 NaNO_3 | 360 NaCl |
| K** | 110 K_2SO_4 | 315 KNO_3 | 344 KCl |

*From [Arendt & Seele, 2001] ** From [Larsen, 1999]

Moisture distribution in the wall, salt concentrations, precipitation, dissolution and formation of new salts vary continually with humidity changes in the surrounding air, the capillary rise of ground moisture and ice formation during winter [von Konow, 2002 B]

Within the structure ion transport and dissolution-crystallization patterns are dependent on the surrounding climate and the salt distribution within the wall will change during the year. Additional there will be a tendency for salt crystallization close to the surface

of the structure dependent of the building material whereas the precipitation height above ground is dependent of the actual salt mixtures solubility.

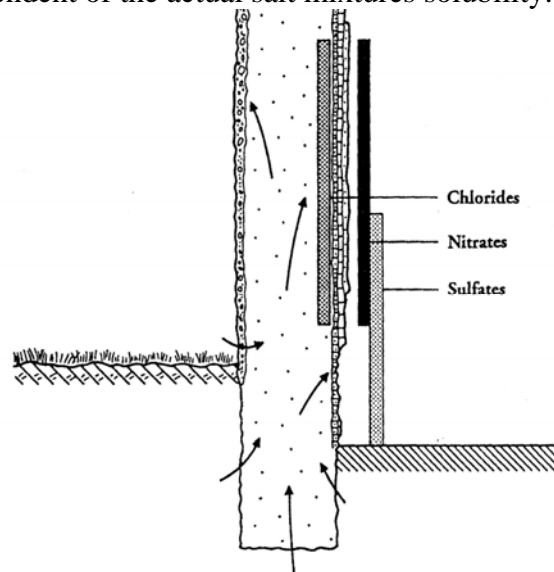


Figure 5. Model of the evolution of salt systems in relation to capillary rise of moisture from [Arnold & Zehnder, 1987].

2. Deteriorating effect of Salts

The crystallization of soluble salts in porous materials can generate pressures inside the pores sufficient to exceed the tensile strength and result in material damage [La Iglesia et al., 1997] visualized in figure 6.

The pressure may be related to different phenomenon:

- Crystallization pressure
- Hydration pressure
- Other theories

The exact pressures from the salt crystals on the pore walls are related to the specific salt [La Iglesia et al., 1997], [Steiger, 2005] and concentrations which determines extend of the salt induced deterioration.

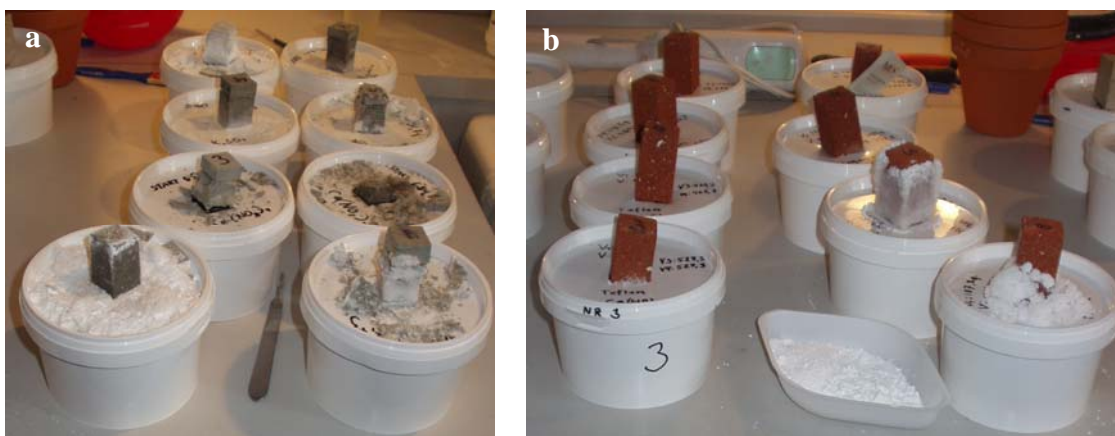


Figure 6. The effect of salt in sandstones and brick specimens (a) Salt induced deterioration of the sandstone specimens mainly crystallization inside the material (b) Visible salt precipitation at the brick specimens surface mainly crystallization on the surface of the material.

2.1 Origin of the salts and their degree of damage

The most common building damaging salts consists of the anions: sulfates, chlorides and nitrates [Perry & Duffy, 1997]. Nitrates originate from conversion of animal stools, biodegradable greenery and is the most traditional ion in dwellings [Arnold & Zehnder, 1987]. Chlorides originate from de-icing salts [Arnold & Zehnder, 1987], sea spray and storage of perishable food [Larsen, 1999]. Sulfates can be present in poorly fired bricks [Lubelli et al., 2004], [Rörig-Dalgaard & Ottosen, 2008B] and originate from air pollution [Arnold & Zehnder, 1987].

Present salt systems, however, consist of many solutes with different properties (e.g. solubility's) and do most probably enter into other combinations than they were added as. The result is that in salt mixtures, salts crystallize at different relative humidity's than for each of the single salts due to a changed equilibrium humidity [Arnold & Zehnder, 1987].

According to Thorborg et al. (2002) the most extensive decay of a test wall was found in relation to sodium chloride and sodium nitrate. In laboratory tests Na_2SO_4 was found to have a deteriorating effect at much lower contents than KNO_3 and K_2SO_4 . Additional sodium- and magnesium sulfate are more destructive than sodium chloride and sodium nitrate [De Clercq, 2008]. In [Rörig-Dalgaard & Ottosen, 2008] was the deterioration process in a painted Monastery vault followed with SEM-EDX analysis and here was the deterioration attributed to the presence of sulfate (gypsum).

In summary is the overall salt system in existing structures very complex regarding formatted salts. The result seems to be differences in the contribution of each salt's deteriorating effect.

2.2 Crystallization pressure

The change from dissolved salt (ions) in solution to nucleated salts is for some chemical compounds connected with a high volume increase. For example the volume of calcium nitrate increases with a factor of approximately 3 during the change from dissolved ions to precipitated salt, (see figure 7) [Arendt & Seele, 2001]. Such volume increase can result in deterioration when the crystallization occurs within the pores of a material.

The most accepted theory for salt induced deterioration describes the crystallization pressure as the determining factor [La Iglesia et al., 1997]. Crypto crystallization (crystallization in the pores of a material) may generate stress, which is termed crystallization pressure [Charola et al., 2007].



Figure 7. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ The volume difference from nucleated state to dissolved state. $2 \frac{1}{2}$ glasses of the nucleated salt fits into 1 glass when dissolved in water [Arendt & Seele, 2001]

2.3 Hydration pressure

The crystallization of salts and their recrystallization from a lower to a higher hydrate during a change in relative humidity may develop a stress of high magnitude termed hydration pressure. The hydration pressure is highly dependent on relative humidity and temperature [Winkler & Wilhelm, 1970].

2.3 Other theories

Not all salts can generate crystallization pressure large enough to cause deterioration. Sodium chloride, for example, develops low crystallization pressure. Material properties (pore size, mechanical strength and moisture transport) and boundary conditions (moisture supply, salt load and distribution as well as environmental conditions) influence the decay pattern and extend. Sodium chloride related damages were shown to be caused by a mechanical interaction between salt and pore wall. The RH changes (and thereby crystal changes) can lead to stresses on the pore wall, in case of adhesion between material and salt [Lubelli, 2006]. Also [Scherer, 1999] relates the degree of deterioration to the surface properties of the porous material described by the contact angle between the crystal and pore walls. Rijniens et al. (2003) showed by Nuclear Magnetic Resonance measurements the difference in destruction degree related to activation of a pressure on pore walls from Na_2CO_3 and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. The Na_2CO_3 activates a pressure on the pore walls contrary to $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and the reason seems to be the difference in the contact angle between the material and the salts.

Larsen & Nielsen (1990) showed that presence of NaCl increases thermal expansion and hygroscopic shrinkage meaning that presence of salts can increase the effect of other deteriorating mechanism.

2.4 The influence of the climate on salt formation

The salt formation and deteriorating effects are among others dependent on climate conditions.

The deliquesce point determines at which relative humidity the change between dissolved salts (ions) in solution to precipitated salts occur. The deliquesce point for some single salts and their variation is shown in table 2.

Table 2. Deliquescence points for single salts from Larsen (1999)

| | Deliquescence point [% RH] |
|---|---------------------------------------|
| $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ | 33 |
| $\text{Ca}(\text{NO}_3)_2$ | 50 |
| $\text{NaNO}_3 \cdot 4\text{H}_2\text{O}$ | 74 |
| NaCl | 75 |
| Na_2SO_4 | 82 |
| $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ | 91 |
| $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | ~100 |

A change in the relative humidity from below to above the deliquesce point result in dissolution of the precipitated salt. Contrary a decrease in the relative humidity from

above to below the deliquesce point results in precipitation of the dissolved salts. Frequently changes in the relative humidity across the deliquesce point induces a dissolution-precipitation cycle within a short period. The result is accelerated salt induced deterioration [von Konow, 2002 B].

At different moisture contents, the ions will crystallize in different shapes and sizes, which are resulting in varying formation pressures. Below a water film, isometric crystals are formed whereas very thin whisker crystals are formatted at a nearly dry surface with a localized solution supply, figure 8 [Arnold & Zehnder, 1987]. The stages (a) and (e) from figure 8 are shown as pictures in figure 9.

Some salts deliquesce point is very dependent of the temperature, and some less (e.g. NaCl). In case of temperature dependent deliquesce point and varying temperature it is difficult to predict whether the salt exist as nucleated salt or dissolved ions at varying climate. Besides traditional studies in laboratory experiments and measurements on existing structures, a new possibility to monitor the deteriorating effect of salts as a function of time is use of time lapse video imaging [Sawdy & Heritage, 2007].

The high complexity of reactions between salt ions in solution, their growth and shape-forming behaviour as well as their reactions with the constantly changing environment makes it almost impossible to find a single correct theory for salt influence on deterioration [von Konow, 2002 B].

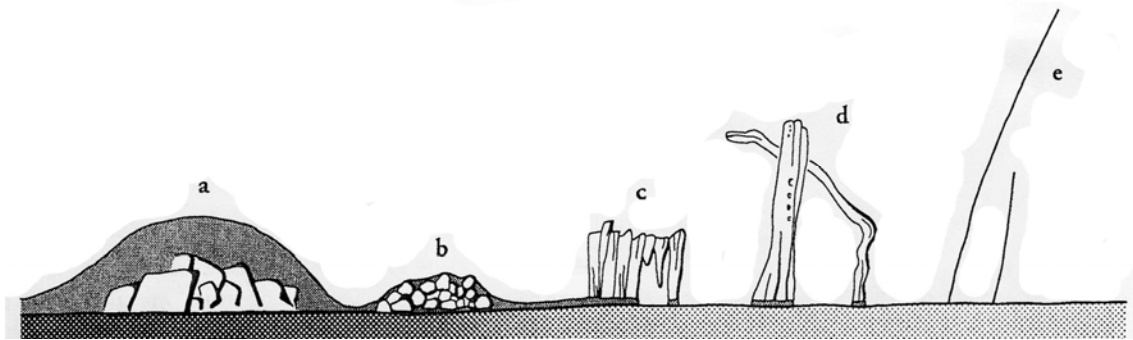


Figure 8. The relationship between crystal morphology and the substrate humidity of a porous material (a) Large crystals, displaying their specific equilibrium forms, grow completely immersed in a solution film on a wet substrate (b) A granular crust made up of smaller and isometric crystals on a wet substrate. The crystals are just covered by a solution film (c) A fibrous crust grows into the air from a substrate surface covered by a thin solution film (d) Columnar and thick whisker crystals grow from a slightly humid substrate; the solution film still forms small spots (e) Very thin whisker crystals grow into the air from the nearly dry surface with a localized solution supply [from Arnold & Zehnder, 1987].

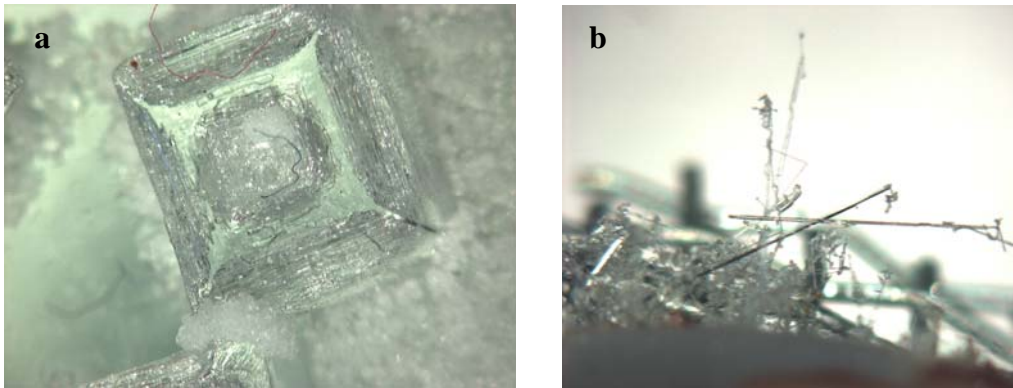


Figure 9. (a) Isometric NaCl formation below a water film (b) NaCH₃COO Whisker crystals formation at a nearly dry surface with a localized solution supply.

3. Damaging salt concentrations in masonry

3.1 Damaging salt concentrations solely related to the salt

At present, there is no threshold value for salt content in masonry in Denmark. Actually very few countries have such threshold values. In Austria a standard ÖNORM 3355-1 is prescribing threshold values solely related to the anions chloride (Cl⁻), sulfate (SO₄²⁻) and nitrate (NO₃⁻), see table 3. The standard suggests (a) limits for unproblematic ion contents, (b) ion contents which in each case have to be considered in relation to restoration need and (3) problematic ion concentrations where reduction in the ion concentrations are advised.

This standard is used in several countries in Europe (Austria, Germany, Denmark). The threshold values outlined in ÖNORM 3355-1 are in general considered as being on the safe side.

Table 3. Threshold values according to ÖNORM 3355-1.

| Anion | Unproblematic content [wt%] | Individual evaluation [wt%] | Problematic content [wt%] |
|----------|-----------------------------|-----------------------------|---------------------------|
| Chloride | < 0.03 | 0.03 – 0.10 | > 0.10 |
| Nitrate | < 0.05 | 0.05 – 0.15 | > 0.15 |
| Sulfate | < 0.10 | 0.10 – 0.25 | > 0.25 |

3.2 Damaging salt concentrations related to salt and material

During the European Project "SCOST" (Fourth Framework Programme, 1998-2001) research was carried out to find threshold values dependent of both material properties and the type of single salt. The investigated salts were: sodium sulfate, magnesium sulfate, sodium chloride and sodium nitrate. The threshold values were found through 4 salt crystallization cycles with a total duration of 20 months. Table 4 shows the results for the two tested substrates an Italian brick and Massangis limestone. Both the substrates (stone type) and the salts were shown to have significant influence on the

threshold values. Further, the threshold values found for single salts were shown to be none describing for systems with mixed salt contents [De Clercq, 2005].

Table 4. Threshold values related to the single salt and substrate from [De Clercq, 2005]

| Substrate | Na ₂ SO ₄ | | NaCl | |
|---------------------|---------------------------------|--------------|-----------------|--------------|
| | No damage [wt%] | Damage [wt%] | No damage [wt%] | Damage [wt%] |
| Italian brick | 0.25 | 0.50 | 0.50 | >0.50 |
| Massangis limestone | 0.12 | 0.25 | <0.50 | 0.50 |

Examination of the ion content in almost 1000 samples from Belgian historic buildings showed that in 13% of the samples only one anion was present (sulfate), in 18 % of the samples a mixture of chlorides and sulfates were found whereas 69% of the samples contained a mixture of chlorides, sulfates and nitrates [De Clercq, 2005]. In a recent investigation of threshold values, threshold values in case of salt mixtures was found complex due to formation of double salts and it was found difficult to predict the behavior of porous materials contaminated with a complex mixture of anions and cations [De Clercq, 2008]. Thus as most salt infected structures have more than one type of salts, it is not possible on basis of concentration measurements alone to predict the danger for severe salt decay.

The previous work in “SCOST”, [De Clercq, 2005], [De Clercq, 2008] pointed out, that the damaging effect is dependent of substrate and actual salt mixture and a systematic research should be carried out for a large range of salts and substrates and combination of these.

In case of salt deterioration of a painted vault in Brarup Church, Denmark, Larsen (2007) observed significant differences in deterioration effect related to the total ion content for all present ions (Na, K, Ca, Mg, Cl, NO₃, SO₄) above and below 0.5 wt%. Below 0.5 wt% of total ions no damage was seen whereas at higher contents deterioration occurred. The same effect was also found in Fanefjord Church, Denmark [Larsen, 2000].

In the present study where desalination of painted masonry was in focus, desalination to below 0.5 wt% of total ions was the first milestone. The second milestone was desalination to threshold values described in ÖNORM 3355-1. However, since the damaging effect of salt is very complex the objective was to reach the lowest possible ion content.

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3. Electrokinetics and its potential as transport mechanism in brick masonry

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Introduction

The idea with the present study was to obtain an increased control with the transport of ions and water within brick masonry. The harmful salt and water in structures have primarily been transported into the structures as dissolved salts (ions) and may cause salt decay. To avoid the decay the salts can be removed again utilizing controlled transport mechanisms.

In the following an introduction to electrokinetics, a group of phenomena for water and ion transport in an applied electric field in porous materials is given. The introduction is related to brick masonry (section 1) and the traditional concentration gradient induced diffusion is compared with electrokinetics (section 2).

1. Electrokinetics

Electrokinetic remediation is a known, documented and well described method for remediation of soil [Alshawabkeh et al., 1999], [Ottosen & Jensen, 2005] [Jensen and Ottosen, 2005], fly ash [Pedersen et al., 2003] [Ferreira et al., 2008], harbour sediments [Nystroem et al., 2005], impregnated wood waste [Christensen et al., 2005] ect. A network dealing with electrokinetic soil remediation (EREM) has existed since 1997, including conferences every second year and since 2008 each year, indicating that the number of researchers and the interest in this area is growing.

Commercial companies in e.g. Austria, Germany and Norway had offered electrokinetic drying and desalination of building structures for several decades, however with limited focus on the documentation of the electrokinetic effects in microscopic scale.

The following introduction to the electrokinetic phenomena is related to building materials.

Electrokinetics deals with the phenomena that occur by application of an electric field across the porous material. The electrical circuit consists minimum of two electrodes, an electrolyte and a fine grained or porous material. In the electrodes the current is carried by electrons and in the electrolyte by ions. At the surface of the electrodes electrode processes transform the current carried by electrons to current carried by ions. See figure 1.

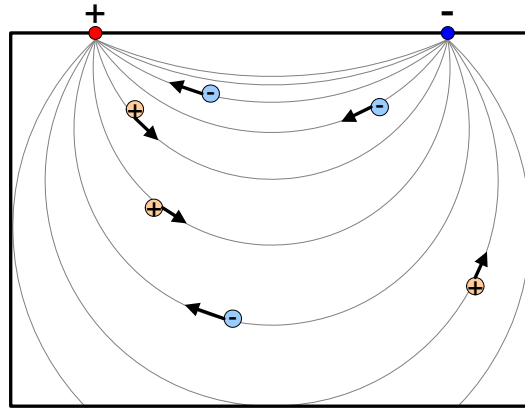


Figure 1. Principle of current distribution in a vertical plane along the line of electrodes with ion migration in a porous material. Freely after van Nostrand (1966).

In this way a controlled transport is possible between the electrodes. In an applied electric field the current will pass where the lowest resistance is (highest conductivity). The effect of the electric field can be divided into two groups: electromigrating ions and electroosmotic water transport. Electroosmosis is dependent on the ion concentration in the pore water.

In the following the electrokinetic phenomena: electromigration (section 1.1) and electroosmosis (section 1.2) are introduced. Additionally are issues of importance for electrokinetic application under real conditions presented (section 1.3).

1.1 Electromigration

For dissolving most precipitated salts of the types causing salt decay only water is needed. When salts like sodium chloride (NaCl) is brought in contact with water it dissolves into the ions sodium (Na^+) and chloride (Cl^-). By application of current to a moist, porous material a positive and a negative electrode are established. Provided that the highest conductivity is in the electrolyte the ions in the electrolyte will start to migrate and be attracted to the opposite charged electrodes, figure 2. This phenomenon is termed electromigration [Mitchell, 1993]. Extraction of the ions out of the pores towards the electrodes as principle is shown in figure 2. At the electrodes where a dry climate exists the extracted ions precipitate and in figure 3 the precipitation of some ions that are extracted from a salt contaminated brick are visualized.

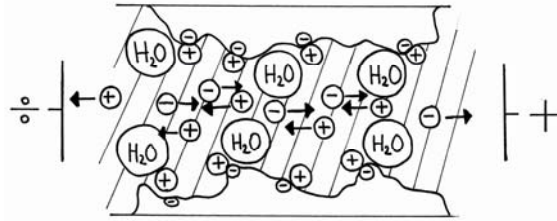


Figure 2. High ionic concentration in the electrolyte shown as a principle for a single pore (the electrolyte is indicated as the hatched area). The ions are attracted towards the opposite charged electrodes in the electric DC field.

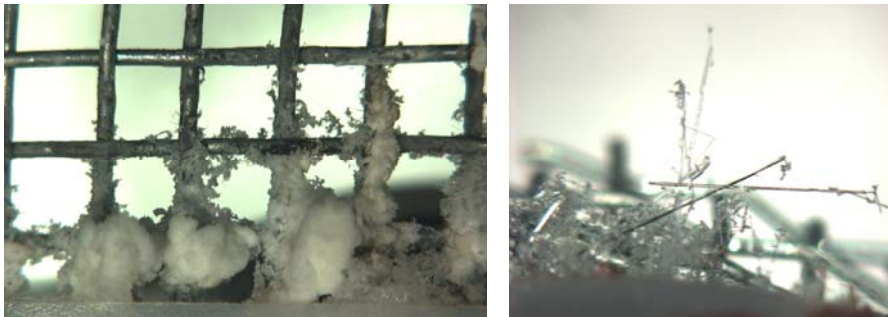


Figure 3. Extracted ions from a porous, salt contaminated material. The salts precipitates at the electrode mesh.

Electromigration (D_0) in a free electrolyte is in Laidler et al. (2003) described as:

$$D_0 = \frac{k_B \cdot T \cdot u \cdot L}{F \cdot |z|} \quad (I)$$

Where k_B is the Boltzmanns constant ($1.3807 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$), T is the temperature (K), u is the ionic mobility ($\text{m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$), L is Avogadros constant ($6.022 \times 10^{23} \text{ mol}^{-1}$), F is Faradays constant ($96485 \text{ C} \cdot \text{mol}^{-1}$) and $|z|$ is the unit charge.

The theory for electromigration related to bricks is further described in [Rörig-Dalgaard & Ottosen, 2008 D] were also the transition between electromigration and initiating electroosmotic water transport for clay bricks were found.

Electromigration in a wall section with murals during a 2 weeks treatment is followed in [Rörig-Dalgaard et al., 2008 E] and showed that the electrokinetic method has the potential for becoming an efficient method for ion transport, provided sufficient moistening can occur (approximately 3-4 wt%).

1.1.1 Consideration of the protection of existing metallic parts

During application of an electric current to a structure with the purpose of dewatering and desalination, special attention has to be taken to presence of metallic parts and stray current effects. Since metallic decomposition occurs at the anode, decomposition can be avoided by introduction of a negative potential, making them to cathodes which is the

principle in cathodic protection. In cathodic protection the steel is polarized to non corrosion condition by changing the sign of the metals potential.

Failure of ensuring all metallic parts could result in local anodic and cathodic sites leading to stray current interactions between the various elements of the structure. This results in accelerated corrosion of the discontinuous items. Just like the potential distribution could be modeled in cathodic protection also stray current effects have been modeled in steel framed brick masonry structures and compared to a sand model to validate and clarify these effects [Lambert, 2007], [Lambert et al., 2005].

Ensurance of that all metallic parts had been applied a current can be carried out by taking them into the system by bonding and/or connection by cable. Accelerated corrosion can also be avoided by electrical isolation of discontinuous metallic parts by replacing fixings with resin-anchors [Atkins, 2002]. Only few constructions e.g. church vaults are without metallic parts and therefore the influence from an applied electric field on the metallic parts must generally be taken into account.

1.1.2 The ion transport velocity in an electric field

Dependent on each ions ease to be transported, ion transport will proceed in a certain order. At equal ionic concentrations, ions with the highest ionic mobility will be transported first, this is related to ion size [Buchwald & Goretzki, 1996] and charge on the ion [Laidler et al., 2003], table 2 and 3. However, H^+ and OH^- ions are primarily transported through proton transfer to its neighboring molecule in water which is at least a factor two higher than traditional ion transport in an electric field [Laidler et al., 2003]. In bricks the following water soluble cations were found by Schumann (1997) and are of relevance for electrokinetic transport: K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} and Fe^{3+} . The ionic mobility's for these are listed in table 1 and 2 together with the traditional damaging anions in structures: NO_3^{2-} , SO_4^{2-} and CO_3^{2-} .

Table 1. Anion mobility for relevant ions [$u/10^{-8}m^2s^{-1}V^{-1}$]

| | OH^- | Cl^- | $\frac{1}{2} NO_3^-$ | $\frac{1}{2} SO_4^{2-}$ | $\frac{1}{2} CO_3^{2-}$ |
|----------------|--------|--------|----------------------|-------------------------|-------------------------|
| Ionic mobility | 20.64 | 7.91 | 5.49 | 4.15 | 3.73 |

[Atkins, 1994] and [www 1]

Table 2. Cation mobility for relevant ions [$u/10^{-8}m^2s^{-1}V^{-1}$]

| | H^+ | K^+ | Na^+ | $\frac{1}{2} Ca^{2+}$ | $\frac{1}{2} Mg^{2+}$ | $\frac{1}{2} Fe^{2+}$ | $\frac{1}{3} Fe^{3+}$ |
|----------------|-------|-------|--------|-----------------------|-----------------------|-----------------------|-----------------------|
| Ionic mobility | 36.23 | 7.62 | 5.19 | 3.09 | 2.75 | 2.74 | 2.39 |

[Atkins, 1994] and [www 1]

The ionic mobilities are given per valence in table 1 and 2, illustrating the effect when one electron is transported between the electrodes.

Provided only H^+ , K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , OH^- , Cl^- , $\frac{1}{2} NO_3^-$, $\frac{1}{2} SO_4^{2-}$, $\frac{1}{2} CO_3^{2-}$, ions are dissolved in the electrolyte, they should be transported according to the following order: $H^+ > K^+ > Na^+ > \frac{1}{2} Ca^{2+} > \frac{1}{2} Mg^{2+} > \frac{1}{2} Fe^{2+} > \frac{1}{3} Fe^{3+}$ and $OH^- > Cl^- > \frac{1}{2} NO_3^- > \frac{1}{2} SO_4^{2-} > \frac{1}{2} CO_3^{2-}$ for cations and anions respectively. Besides the ionic mobility each ions actual concentration in relation to the total concentration also is determining for the transport order.

Consistence between theoretical ionic mobility [Atkins, 1994] and empirical obtained results has been shown, since increased ion transport was observed for ions with the

highest theoretical ionic mobility. Ottosen & Rörig-Dalgaard (2008 B) observed that K^+ ions moves faster than Na^+ ions in bricks and Fajardo et al. (2006) and Ali et al. (1992) observed that K ions moves faster than Na, Mg and Ca in concrete.

Additional [Ottosen et al., 2001B] found the following order of cation transport $Ca > Mg > Fe$ in soil.

However, during the electrokinetic process electroneutrality must be present all the time. This means that e.g. an anion will be limited by the velocity of the fastest cation. Buchwald & Kaps (1999 B) found a higher transport coefficient for Na^+ in a NaCl ($2.3-3.8 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$) solution than in a Na_2SO_4 ($1.4-2.4 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$) solution by diffusion in bricks. The necessity of electroneutrality all the time and its effect on the transport of single ions was shown by use of electromigration in Ottosen & Rörig-Dalgaard (2008 B). The results showed a higher transport rate of Cl^- added as KCl than for Cl^- added as NaCl which is in consistence with the values in table 2.

1.2 Electroosmosis

In the pore solution, ions with the same sign as the dominant charge at the material surface (co-ions) are repelled from this and ions with the opposite sign as the surface charge (counter-ions) are attracted. At equilibrium conditions the net charge density at the material surface must be equalized in magnitude and opposite in sign. This equilibrium exists within a small distance from the inner material surface where the volume called the electric double layer is divided into a fixed part and a non-fixed part (termed the diffuse layer) [Revil et al. 1999]. At low electrolyte concentrations, the conductivity throughout the system is highest in the electric double layer, however a small and non determining ion concentration is also present in the diffuse part of the electric double layer. Since the co-ions are fixed, a net flow of counter-ions will occur towards the opposite charged electrodes in the diffuse part of the electric double layer, causing turbulence in the surrounding water and resulting in a net water transport, termed electroosmosis [Mitchell, 1993]. See figure 4 (a) for a sketch of the phenomena and 4 (b) shows the transported water to the cathode in a pilot scale experiment for drying of masonry.

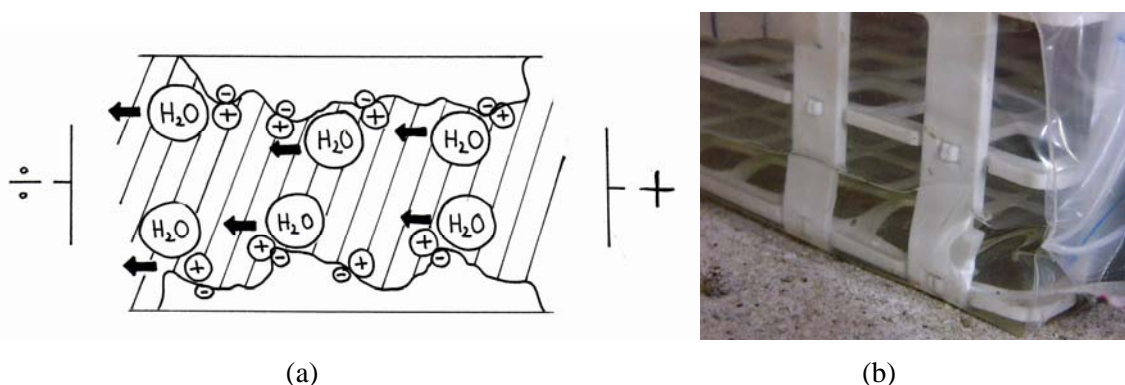


Figure 4. Low ionic concentration in the electrolyte. By application of an electric DC field water transport is initiated close to the material surfaces (in the diffuse part of the electric double layer). (a) A principle sketch (the electrolyte is indicated as the hatched area) (b) The electroosmotic water transport effect shown in pilot scale. The collecting unit with water below the cathode [Ottosen & Rörig-Dalgaard, 2006].

Effectively, electroosmotic water transport towards the negative electrode (cathode) has been observed for most porous materials [Ottosen et al., 2008].

According to Helmholtz and Smoluchowskis theory the electroosmotic water transport velocity (v) can be described as:

$$v = \sigma \cdot \frac{\delta \Delta E}{\eta \Delta L} \quad (\text{II})$$

Where σ is the surface current density, δ the thickness of the electric double layer, η is the viscosity, and $\Delta E/\Delta L$ is the size of the applied electric field per area [Mitchell, 1993].

The surface current density is dependent of the actual material and was found to vary a factor 2 between different brick types (varying in color and age) [Rörig-Dalgaard & Ottosen, 2008 D]. The thickness of the electric double layer depends on the electrolyte concentration where increasing electrolyte concentrations results in decreased thickness of the electric double layer. The viscosity depends also of the composition of the electrolyte. The maximum applied electric field and thereby the current density, which is not related to practical problems seems among others to be limited to the total resistance in the system.

In summary is the only external determined parameter the applied electric field and therefore the focus during optimization by taking other parameters into account.

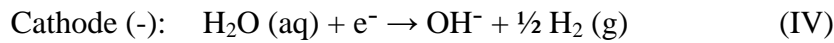
Use of pulsed electric field current could be an optimization possibility as used by Rojo et al. (2005) to improve the copper removal from mine tailings. During application of an electric DC field a concentration gradient is formed as ions with the same charge moves towards the same electrode and the diffusion gradient prefer ions transport in the other direction. This induces unbalance in the system and reduces the effect of the applied electric field. By turning of the electric field for a shorter period, a part of the concentration potential is reduced and thereby the efficiency increases. Especially in connection with electroosmotic dewatering use of a pulsed electric field is expected to be efficient. The major part of the counter ions moves towards the cathode and thereby a significant concentration gradient develops.

It must be noticed that electroosmotic dewatering is not initiated in bricks and masonry before a low ionic concentration in the pore solution is obtained. In bricks the concentration where electroosmotic dewatering is initiated was experimentally found to 0.01 wt% Cl in a brick that was contaminated with NaCl. However, this concentration may vary between different brick types and contaminating ions [Rörig-Dalgaard & Ottosen, 2008 D].

1.3 Electrode reactions and pH changes

The transformation of the current carried by electrons in the electrodes to the current carried by ions in the pore solution and visa versa is termed electrode reactions. In case

of inert electrodes and low concentrations of ions in the electrolyte the primary reactions will be [Acar, 1993]:



This will result in varying formation of acid (H^+) and base (OH^-) dependent of the applied electric field, the duration and basically of the total current consumption and thereby produced H^+ and OH^- .

Additionally, the effect of the electrokinetic phenomena will most properly decrease as the current will transport H^+ and OH^- instead of the wanted ions when present, since H^+ and OH^- has exceptionally high ionic motilities (section 1.1.2). Reduced transport number and thereby also chloride transport has been measured during desalination of concrete with electromigration and this was mainly attributed to the OH^- generation and the higher mobility of the hydroxyl ion. This implies a limit in the amount of extraction and complete chloride removal is impossible if no action is taken against this OH^- generation when dealing with concrete [Castellote et al., 2000].

In case of additional ions (e.g. chlorides) in the vicinity of the electrodes, these can dependent upon the concentration of available species take part in the electrode processes. E.g. presence of chloride and non inert electrodes can result in the following reactions at the anode:



An example of decomposition of a corroding anode is shown in figure 5. Additionally the decomposition can result in discoloring of the adjacent material with the decomposed metallic ions. Especially iron anodes, which results in a red color.

Also precipitation of hydroxides can occur in the vicinity of the cathode.

For assessment of the influence of the electrode reactions on the surrounding materials a constant current is preferable since the electrode reactions occurs proportional to the applied current. Therefore will use of a constant current ease the calculation of formatted electrode products. However, since several reactions may take place parallel, the precise formation of a specific component can be difficult to assess.



Figure 5. Decomposition of the anode mesh made of stainless steel. The original metallic gray color is during the decomposition changed to black and later green and the metal mesh will subsequently get so deteriorated that it breaks. Stainless steel is surface coated iron.

In summary uncontrolled electrode reactions can result in pH changes, discoloring of the surrounding materials and decreasing efficiency. This makes the electrode reactions to an essential parameter in praxis.

1.4 Matrix changes

If no precautions are taken to protect the structures against the acid and base produced at the electrodes during the electrode reactions, pH of the masonry will change. Exposure of acid to ceramic material (roofing tiles) has resulted in increased porosity [Radeka, 2007] and thus acid is known to damage the ceramic material. Castellote et al. (1999) found an indication of an increase in the total porosity in concrete after an electrochemical treatment.

During the lifetime of a masonry structure, pH changes in the bricks. In Rörig-Dalgaard & Ottosen (2008 C) a reduced pH was measured in older bricks and especially in older exposed bricks. Since the electrode reactions at the anode results in acid (H^+) production and thereby continuously pH decrease during treatment, application of an uncontrolled electrokinetic system seems to result in an accelerated weathering. This is in good consistence with Ottosen et al. (2008) which describes acidification of soil as accelerated weathering. A controlled electrokinetic system must be established to avoid this accelerated weathering.

In Rörig-Dalgaard & Ottosen (2008) precautions were taken against these electrode processes by introducing a poultice with buffer components between the masonry and the electrodes. In Appendix 1 further developments of the cathode poultice to a three layer poultice is described. This development resulted in the patent application 08154186.4.

1.5 Material dependence

Ion transport equations for liquids cannot be used directly in porous materials since ion transport in a porous material is dependent on the pore distribution, structure and size, as well as the saturation degree [Buchwald & Goretzki, 1997], [Vogt & Kriegel, 2005], [Buchwald & Kaps, 2000] and the electrolyte concentration [Truc et al., 2000]. Buchwald & Goretzki (1997) found the free diffusion in a liquid to be approximately a factor 10^5 higher than in a saturated brick. In addition, the relative diffusion velocity for different ions in bricks was consistent with the order found for free diffusion in a solution (table 1+2).

Actual measured ion transport in a porous material in steady-state conditions is termed effective diffusion. Truc et al. (2000) suggested a material dependent link between traditional diffusion (D_0) in a free solution and the effective diffusion (D_e) in a porous material:

$$D_{\text{eff}} = p \frac{\varepsilon}{\tau} D_0 \quad (\text{VII})$$

Where p is the porosity, τ is the tortuosity (the increase in effective diffusion road) and ϵ the constrictivity (the resistance on the ion transport from narrow pores determined on the proportion between ion and pore diameter, always below 1).

Bricks vary in e.g. porosity, density, capillarity, saturation degree related to firing degree and this influences the effective diffusion coefficient and electric resistance across a material. In bricks it was shown that many tiny pores in poorly fired bricks favors the electromigration efficiency compared to fewer larger pores in hard fired bricks [Rörig-Dalgaard & Ottosen, 2008B]. The environmental exposure of bricks can have major impact on the ionic content and therefore result in significant a difference [Rörig-Dalgaard & Ottosen, 2008C] which again affects the overall resistance and need for desalination.

1.6 Changing experimental conditions

For optimization in laboratory scale different experimental conditions can be varied. E.g. Pedersen (2002) and Nystrøm (2004) optimized the applied current strength in laboratory scale for fly ash and harbour sediments, respectively, in order to optimize the heavy metal removal. Optimization of an electrokinetic system depends on the actual material or mixture and purpose of the treatment.

An increase in applied electric field can reduce the duration of the action and in some cases be preferred to minimize secondary effects (e.g. evaporation). Contrary, an increased electric field by use of constant current density results according to ohms law ($U = R \cdot I$) in a higher voltage drop across the setup and the total resistance throughout the system will increase at an increased electric field and result in increased heat formation.

During desalination of a wall section [Rörig-Dalgaard et al., 2008 E], limited water supply was accepted to avoid microbial growth. This resulted in a higher total resistance than in capillary saturated bricks and a lower possible constant current. Therefore, one of the limiting experimental conditions seems to be the overall resistance in the system.

2. Comparison of transport by diffusion and electromigration

In the following some comparing experiences with diffusion and electromigration are described on basis of theoretical equations in order to assess the ability of electromigration as transporting process.

Diffusion occurs primarily due to concentrations gradients, and therefore the differences in electrolyte concentration are the domination factor [Laidler et al., 2003]. The diffusive flux (J) is defined in Laidler et al. (2003) and described as:

$$J = -DA \frac{\partial c}{\partial x} \quad (\text{VIII})$$

Where D is the diffusion coefficient, A the area through which the ions pass and $\partial c / \partial x$ is the concentration gradient of the solute.

Electromigration occurs primarily due to differences in the potential. The migrational flux (J_j^m) is defined as [Acar & Alshawabkeh, 1993]:

$$J_j^m = u_j^* \cdot c_j \cdot -\frac{\partial E}{\partial x} \quad (\text{IX})$$

Where u_j^* is the effective ionic mobility, c_j is the molar concentration and E is the electrical potential per distance between the electrodes.

Buchwald (2000) showed experimentally a significant accelerated ion transport by electromigration compared to ion diffusion in the range of a factor 1.5 by application of 100 V/m in non optimized setups. Additional, it must be noticed that electromigration is dependent of the size of the applied electric field (see equation IX) and optimization of the electrokinetic process and a much higher factor between electromigration and diffusion is therefore likely. The obtained electromigration velocities do therefore only show the velocity in the actual applied field. An increase in applied electric field at constant concentration in the pores results in an increase in the velocity at which the ions are transported.

Buchwald & Goretzke (1996) made comparing experiments between electromigration and diffusion from bricks out in a compress plaster. The experiments showed a 50-70% reduction of the original ion content within 6 days with an applied voltage of 5 V. Whereas a 30 % reduction was found in the diffusion experiments after 3 weeks and an elongation of the treatment duration without applied current did not result in significant higher salt extractions. The authors concluded that considerable higher salt extraction can be obtained by electromigration than by diffusion. Additionally, the direct action of ions during electrokinetic treatment likely less pore clogging by electromigration than by diffusion. It is also likely that necessary water content before the ion transport is initiated is lower in relation to electromigration than to diffusion.

Final comment

Use of an applied electric field for desalination by electromigration and electroosmotic drying seems to have a potential for controlled transport in porous materials. The advantages are both the direct influence on the ions and the ability to increase the transport velocity.

However, for optimization in laboratory scale and in praxis several parameters have to be taken into account: applied field, water content, electrode processes, material parameters, ionic mobility and possible matrix changes. A wide knowledge by the executer is therefore essential before the method can be applied to existing structures and especially before application to cultural heritage.

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[www 1] http://web.med.unsw.edu.au/phbsoft/mobility_listings.htm

The environmental effect and the colors influence on soluble ions in bricks

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Abstract

Brick masonry is affected by different environmental factors e.g. acidic rain. The effect of the exposure on bricks was investigated in the present paper on a variety of bricks: new & old (related to location and exposure), red & yellow and manufactory procedure (tunnel oven, circular kiln). The effect and extend from environmental influence is measurable on the amount of soluble ions and pH.

Preparation of brick and clinker samples has previously been carried out according to the standard DIN 38 414 (S4) elaborated for examination of water, waste water and sludge materials and due to the standards application area series of experiments were carried out in the present work to test the standards applicability on bricks. Use of the standard resulted in satisfying reproducible, robust measurements and was subsequently used for the present investigations.

The total content of soluble ions verified both by the electrical conductivity measurements and as a sum of the actual anion and cation measurements clarified significant variations between bright, medium and dark colored brick. Also significant differences in contents of soluble ions were found related to red/yellow color, location and age.

Resistance against acidification of bricks was only found in a yellow brick whereas alkali resistance was absent both for red and yellow bricks.

The pH of a variety of bricks showed major differences related to exposure and a lower pH was shown in the bricks that had been a part of masonry for many years compared to new bricks. Both the environmental exposure and the color of the brick had significant influence on the content of water extractable ions in the bricks.

Keywords

Bricks, color variation, firing temperature, amount of soluble ions, pH, acid resistance, alkali resistance, environmental influence

1. Introduction

Building components, including bricks are affected by different environmental factors e.g. acidic rain [Schumann, 1997]. The pH is changed at the surface of the bricks when the newly build brick masonry is washed with acid to remove excess mortar. The methods for electrokinetic desalination and water transport can also be connected with pH changes [Demberger, 1991], [Auras & Melisa, 2002] if no precautions are taken. However, pH stability is possible during electrokinetic treatment [Rörig-Dalgaard & Ottosen, 2008].

The environmental effect on the soluble ions in bricks is in the present paper illustrated through a variety of different Danish bricks: new and old, yellow and red.

New manufactured bricks are expected to have little variation due to modern manufacturing methods, contrary to ancient bricks. The variation in soluble ions caused by ancient manufacturing methods was investigated. Only in few cases original clay and burned clay bricks have been found and used for material characterization as in [Larsen, 2007]. [Larsen, 1996] showed similar properties between the brick type Falkenløwe made for restoration purpose (handcrafted and fired in a circular kiln [www.Falkenloewe.dk]) and original medieval bricks regarding: density, porosity, pore size distribution and capillary suction. The Falkenløwe brick is due to its material properties, size and look used when replacement in ancient Danish buildings is necessary e.g. in Sct. Maria Church in Helsingør, Denmark, figure 1. Falkenløwe red brick was for this reason chosen as representative for ancient bricks in the present work with possibility for reproduction of measurements.

Beside the Falkenløwe brick, traditionally produced bricks, bricks located at typical locations and with typical environmental exposure in Denmark were investigated to determine the influence of these different factors and their level.

The aim of the work was to find the environmental influence regarding pH and the exposure to the environment on the soluble ion content measured as a total by electrical conductivity measurements and the soluble ion content in general for a variety of Danish bricks. The firings influence on the content of soluble ions (SO_4 , NO_3 , CO_3 , Cl , Fe , Ca , Mg , K , Na) was investigated for the brick type Falkenløwe red.



Figure 1. Picture of the pillar to the right of the altar in Sct. Mariæ Church, Helsingør, Denmark. Replacement with Falkenløwe bricks of deteriorated bricks have been carried out. Color variation is visible.

2. Materials and methods

2.1 Materials

The variation between new and old, red and yellow Danish bricks was searched related to color and exposure. The amount of soluble ions and the environmental effect was investigated for different brick types with different ages and locations (in building constructions and with full weathering exposure on the ground). For the purpose were two new red bricks (Wewers red and Egersund), a new yellow brick (Wewers yellow), a new brick made for restoration purpose (Falkenløwe) with colors varying from bright and medium to dark, and three sorts of old bricks which was subjected to varying exposure (Gl. Amtsvej 5, Gl. Amtsvej 7 and Æbleholt) examined. An overview of the bricks is given in table 1.

Table 1. Overview of bricks for the investigation.

| Name | Color | Age | Location |
|--------------------|------------|----------------|--|
| Falkenløwe, bright | Bright red | New | Factory |
| Falkenløwe, medium | Medium red | New | Factory |
| Falkenløwe, dark | Dark red | New | Factory |
| Æbleholt, bright | Bright red | App. 800 years | West to Hillerød. Collected from the ground (agricultural field) |
| Æbleholt, medium | Medium red | App. 800 years | West to Hillerød. Collected from the ground (agricultural field) |
| Brarup Church* | - | App. 700 years | On top of a Church vault. Probably leftover from the time of construction Below a thick layer of clay |
| Gl. Amtsvej 7 | Red | App. 100 years | Basement |
| Gl. Amtsvej 7 | Yellow | App. 100 years | Basement |
| Gl. Amtsvej 5 - A | Yellow | App. 70 years | Unheated annex, the last 2 ½ year placed on the ground - visible weathered |
| Gl. Amtsvej 5 - B | Yellow | App. 70 years | Unheated annex, the last 2 ½ year placed on the ground - not visible weathered |
| Wewers yellow | Yellow | New | Factory |
| Wewers red | Red | New | Factory |
| Egersund | Red | New | Building site - wrapping newly opened |

* from [Larsen, 2007]

Falkenløwe brick is a new brick made for restoration purpose, fired in a circular kiln with obvious color variations: bright, medium and dark.

Æbleholt bricks are approximately 800 years old bricks from the monastery ruin in Hillerød (found at the ground) which had similar colors like Falkenløwe bricks: bright and medium red. However, it is unknown whether the bricks originate from the erection of the structure.

Gl. Amtsvej 7 red and yellow bricks are traditional Danish bricks. They have been in the masonry of a basement for approximately 100 years. Mixing of red and yellow

bricks in constructions in non visible areas was very common in Denmark at the time of construction.

Gl. Amtsvej 5 is also a presumable typical yellow Danish bricks, until 2 ½ year before the measurement were carried out situated in an unheated annex and subsequently 2 ½ year situated on the ground. Brick A is extensive deteriorated whereas brick B is without visible deterioration on the surface.

Wewers yellow, Wewers red and Egernsund red are typically new bricks used for construction of new buildings. Comparisons were made with a fired clay brick found in Brarup Church, Denmark, most likely left over from the construction of the vault around 1300 AC [Larsen, 2007].

2.2 Methods

2.2.1 Sample preparation

In connection with bricks and clinker the standard DIN 38 414 (S4) has previously been used for preparation of samples for Na, Cl, SO₄ measurements [Buchwald & Goretzki, 1996]. The standard is elaborated for examination of water, waste water and sludge. The area of application is also solids, paste-like and sludge's.

To test the standards applicability on bricks regarding sample preparation for electrical conductivity and pH measurements similar relations between dry material (5.00 g powdered brick) and distilled water (12.50 mL) was used as in the standard DIN 38 414 (S4). The goal was to find a robust measurement method for the electrical conductivity and pH, where an approximate equilibrium value (representing ended reaction between brick powder and liquid) is reached and thus having a method being limited time sensible. In series (a) frequently measurements were carried out in the beginning (after ½, 1, 1 ½, 2, 2 ½, 3, 3 ½, 4, 4 ½, 5, 5 ½, 6, 6 ½ and 7 hours) where relative big changes were predicted and later in test periods (at 24, 24 ½, 25, 25 ½ and 48 hours) as almost no change was assumed. In series (b) solely measurements after ½, 24 and 48 hours were carried out since absence of air supply was assumed to result in limited changes, figure 4 and 5. Disrupted agitation time results in frequently air supply whereas continuously agitation remained a relative air tight system.

The pH was measured with electrode MeterLab® CDM220 and the electrical conductivity with electrode MeterLab® CDM210 after settling of the agitated sample (for 5 minutes or until a clear liquid came into existence).

2.2.2 Anion measurements

For chloride, sulfate and nitrate measurements 5.00 g brick powder was added to a 12.50 mL solution of distilled water and agitated for 24 hours. The chloride content was subsequently measured by a titrator (Metrohm 716 DMS Titrino) and sulfate and nitrate was measured with ion chromatograph.

2.2.3 Cation measurements

Samples with 10.00 g brick powder and 25.00 mL distilled water were agitated for 24 hours. Subsequently the cation concentration was measured with AAS. This means the same liquid to solid ratio was used as for the anions measurements.

2.2.4 Acid and base resistance

The acid soluble part of carbonate was determined by a volumetric method [Loepperts & Suarez, 1996] where 2.5000 g powdered brick reacted with 20 mL 10% HCl to CO_2 and the developed air volume revealed the content.

For determination of the acid and base buffer capacity, suspension of 5.00 g dry powdered brick was added to 25.00 mL HNO_3 with the concentrations: 0.01, 0.05, 0.1, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0 M. The samples were agitated for: 1, 5 and 24 hours and pH subsequently measured. The investigations with acid are similar to the investigations in [Ottosen & Rørig-Dalgaard, 2007]. Additional measurements were carried out to find the base resistance by use of the strong base NaOH.

3. Sample preparation

The results from the two experimental series with and without air supply are shown in the figures 2 and 3.

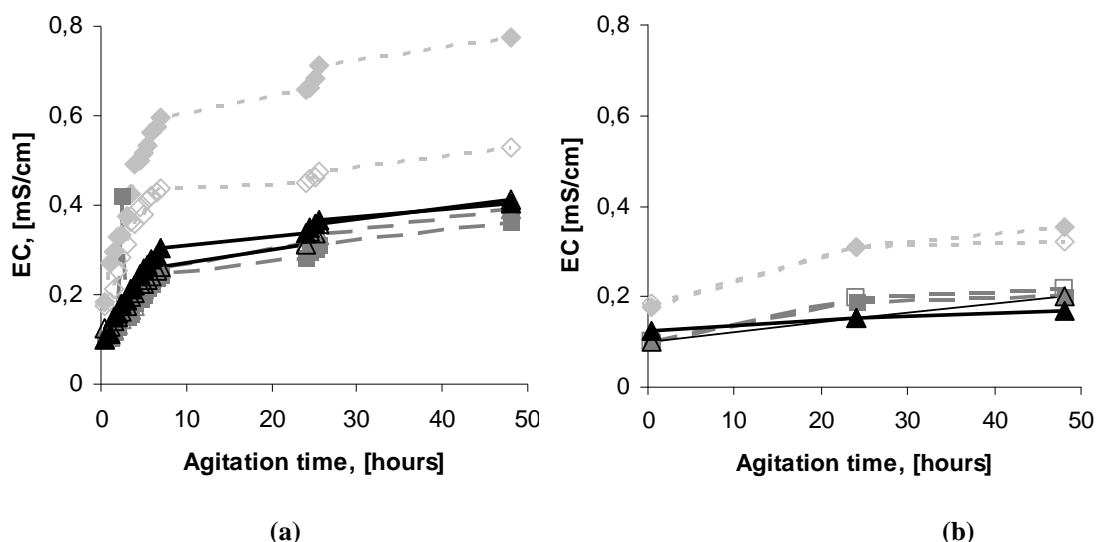


Figure 2. Double determination of the total electrical conductivity (EC) measured in the bright \blacklozenge , medium \blacksquare and dark colored brick \blacktriangle (a) with opening/closing of the samples (air supply) and (b) without opening/closing of samples (air supply).

Both by disrupted (air supply) and continuous shaking (without air supply), significant differences in the measured electrical conductivity between bright, medium and dark colored bricks were measured, figure 2. This higher conductivity in the bright colored brick is attributed to a higher ionic content in the bright colored brick.

In addition a significant increase was found between the measurements after half an hour and 24 hours, whereas only minor increase was measured between 24 and 48 hours in both cases.

The difference between the measured values for bright, medium and dark colored bricks in the two series suggests that the measured differences are a result of both color variation and differences in the reaction with distilled water.

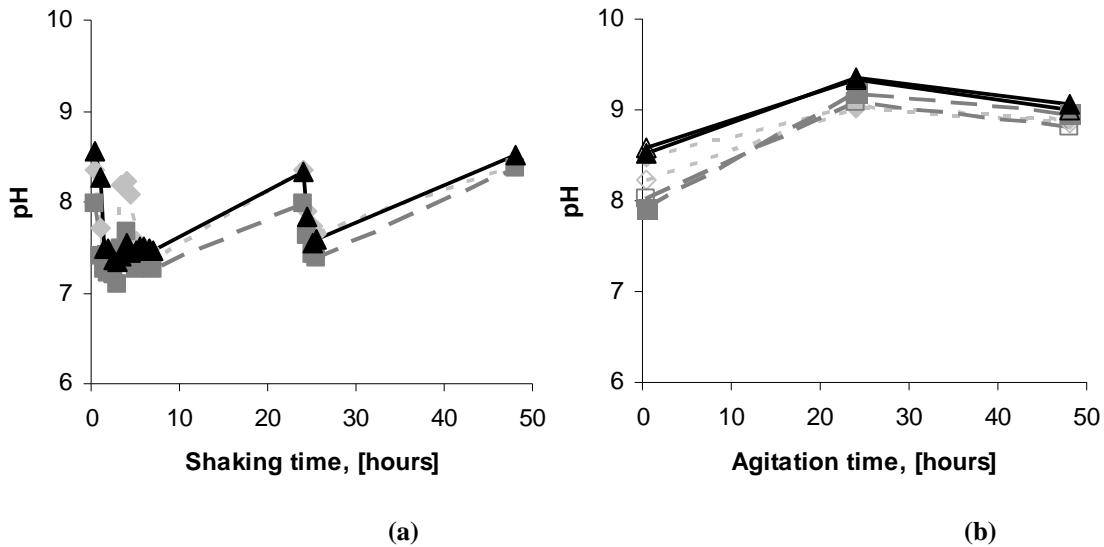


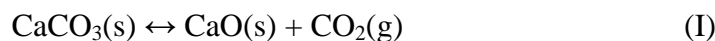
Figure 3. Double determination of pH measured in the bright \diamond , medium \blacksquare and dark colored brick \blacktriangle (a) with opening/closing of samples (air supply) and (b) without opening/closing of samples (air supply).

In figure 3, the difference between the measured pH of bright, medium and dark colored bricks is decreasing throughout the two experimental series. After ½ hour agitation a difference of 0.5 in pH was measured (between medium and dark colored brick), after 24 hours the difference was 0.2 (between bright and dark colored brick) whereas no significant difference was measured after 48 hour agitation time.

In the experimental series (a) with frequently air supply stable pH values was measured after 1½ hour. Meanwhile after 24 hours (17 hours undisturbed, air tight agitation) the pH had increased and first after 3 openings of the samples, the same pH values as after 1-6 ½ hour was obtained. The same pattern with increased pH after undisturbed agitation was observed after 48 hours. In series (b) the maximum value was obtained after 24 hours. Some variation between bright, medium and dark colored bricks was still evident.

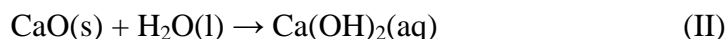
The difference between measurements with disrupted and continues agitation both in electrical conductivity and pH suggest that the air contact influences the result as the temperature (which could also affect the result) was fairly the same. The influence of the air contact on the measurements is especially clear in the measurements of electrical conductivity after 24, 24 ½, 25 and 25 ½ hours (figure 2). Here the same steep increase is seen as measured within the first hours.

Calcium connections in bricks changes during manufacturing and the bricks lifetime. Calcium is most often present as calcite (CaCO_3) in many clay types [Schumann, 1997]. By firing of clay, Calcite starts to get decomposed to lime (CaO) and carbon dioxide (CO_2) [Chang, 2005]:



According to [Schumann, 1997] this occurs at temperatures higher than 900°C , whereas [Cultrone et al., 2001] describes almost fully transformation into burnt lime (CaO) at temperatures between 830°C - 870°C . Thus there seems to be some disagreement about the exact temperature for the transformation.

By presence of moisture the burnt lime reacts readily to calcium hydroxide [Elert et al., 2003]:



And by presence of atmospheric carbon dioxide calcium hydroxide eventually reacts to calcite [Elert et al., 2003] which is termed carbonization [Gottfredsen & Nielsen, 1997]:



Reaction (I) had most probably occurred in the fired bricks. Reaction (II) occurs by mixing of the powdered brick and water whereas reaction (III) initiates during the measurements as a consequence of CO₂ supply from the air by opening of the samples for measurements.

Therefore carbonization (reaction III) of the powdered brick material (which possesses significant increased surface area due to the powdering) is the most likely process leading to pH decrease in the presence of air supply in figure 3.

Contact between water and carbon dioxide results instantaneously in carbon dioxide absorption ($\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$). At pH between 6.3 and 10.3 carbonate is mainly present as HCO_3^- ($\text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+$) [Harremoës et al., 1989] which contributes to the electrical conductivity. By frequently air supply the HCO_3^- content will become a major influence and on the measured electrical conductivity and this is suggested to be the difference in measured electrical conductivity with and without air supply showed figure 3

Since the carbonization first occurs during the measurements and not naturally in the brick (despite of as a function of decades) and increase in the electrical conductivity only occur during frequently air supply after powdering, the most representative way to prepare the samples must be to carry out undisrupted agitation to avoid air access. Series (a) in figure 3 seems therefore to be pH measurements of carbonization as a function of time.

It seems like both the electrical conductivity and pH measurements are robust and reproducible when carried out after 24 hours undisrupted agitation (without air supply) as described in the standard DIN 38 414 (S4) and the samples were therefore prepared as such in the following.

4. Chemical differences related to the colour

In this section the brick type Falkenløve is discussed in what regards the amount of water soluble ions related to brick color. In a pallet with 200 red Falkenløve bricks significant color variations was seen (figure 4) corresponding to the color variations seen by replacement in existing constructions figure 1. The hypothesis is that the color variation is a consequence of different firing temperatures rather than difference in raw material. According to [Schumann, 1997] the color is dependent of several parameters (atmosphere, firing temperature, CaO content in



Figure 4. Color variation from a pale of Falkenløve bricks: Dark, medium and bright.

the clay composition etc.) and the color as determination method for firing temperature can therefore only be used in case of exactly the same clay mixture. As the bricks used in this paper are of the same sort, from the same company, from the same pale it is most likely that the difference in color is related mainly to differences in the firing temperature. According to [Rasmussen, 1992] are orange colored bricks fired at 800-900°C whereas higher firing temperatures results in more intense red colors.

The Falkenløwe bricks are fired in a circular kiln [www.falkenloewe.dk] where the heating source is placed in the middle of the oven with different brick firing temperatures dependent of the bricks position in the oven. The result is differences in colors (bright, medium and dark). The hypothesis is that the color variation seen in the pale with 200 Falkenløwe bricks is caused by differences in firing temperatures. The manufacturing procedure of Falkenløwe gives an infrequent insight in the firing temperatures influence on the amount of soluble ions in the bricks related to firing temperature. Contrary to bricks produced in a circular kiln, modern bricks are manufactured in a tunnel oven with evenly distributed temperature for production of bricks with as little variation as possible.

In the following the anions: Cl, SO₄, NO₃, CO₃ and cations: Na, Mg, Ca, K, Fe are found for the bright, medium and dark colored brick and compared with Wewers yellow.

4.1 Anion content

Evaluation on damaging salt content is traditionally related to the anions SO₄, Cl, NO₃ e.g. ÖNORM B 3355-1 and these are the anion included in the present investigation (see table 2). Significant changes with CO₃²⁻ occur during firing and its chemical reaction is therefore also described.

Table 2. Anion content for different brick types.

| Brick type | SO ₄ ²⁻ [mole/kg] | Cl [mole/kg] | NO ₃ ⁻ [mole/kg] | Sum of measured anions [mole/kg] | Sum of measured anion content [mole/L]** |
|-------------------------------|--|------------------------------------|---|---|--|
| Falkenløwe Bright (triple) | 0.002735 +/- 1.3 e ⁻³ | 0.000337 +/- 2.3e ⁻⁵ | 0.000053 +/- 9.5e ⁻⁷ | 0.00313 | 0.00125 |
| Falkenløwe Medium (triple) | 0.001513 +/- 6.0e ⁻⁴ | 0.000337 +/- 2.8e ⁻⁵ | 0.000052 +/- 9.1e ⁻⁷ | 0.00190 | 0.00076 |
| Falkenløwe Dark (triple) | 0.001362 +/- 3.8e ⁻⁴ | 0.000309 +/- 2.7e ⁻⁵ | 0.000053 +/- 1.3e ⁻⁶ | 0.00172 | 0.00069 |
| Wewers yellow (dobble) | 0.001275 +/- 1.1e ⁻⁵ | 0.000243 +/- 1.1e ⁻⁵ | 0.000079 +/- 5.9e ⁻⁸ | 0.00160 | 0.000639 |
| Brarup Church, fired* | - | 0.08 | 0.01 | 0.09 | × |

* from [Larsen 2007] – below the detection limit of 0.01 mole/kg × not possible to convert

** mole/L is calculated on basis of the added liquid for the measurements and used in section 4.3

Bricks fired at a low temperature have a very bright red color and higher concentrations of sulfate than brown and light orange bricks [Lubelli et al., 2004]. Charola (2002) also describe decreased contents of sulfate (present as sodium sulfate) at increased firing temperatures in bricks. The melting point of Sodium sulfate (Na₂SO₄) is 884°C [Weast, 1983]. After melting a changed conductivity must be expected as the previously sodium sulphate properly will take part in the glass matrix in another form than sodium sulfate. According to [Schumann, 1997] occurs oxidization of sulfides in the original clay during firing. The measured sulphate content was significantly higher in the bright

colored brick than in the medium and dark colored brick which support the theory of one single melting point, see table 2.

Contrary, no significant difference between bright, medium and dark colored bricks was measured related to the nitrate and chloride content.

The total measured anions in Falkenløwe bright, medium and dark were within the same range. Meanwhile the sum of the measured anions was significant higher for bright than for medium and dark. The measurements showed magnitudes of difference for the measured anions $\text{NO}_3^{2-} < \text{Cl}^- < \text{SO}_4^{2-}$ ($\text{NO}_3^{2-} * 200 \approx \text{Cl}^- * 100 \approx \text{SO}_4^{2-}$). Compared to Wewers yellow brick, Falkenløwe red brick contained higher sulfate and chloride but lower nitrate and chloride contents. The Brarup church brick had relative high contents of chloride and especially nitrate. This differs pronounced from the contents in the other bricks.

4.2 Cation content

Screening of an original brick from the Carmelite monastery in Helsingør and of a new Falkenløwe red brick by SEM-EDX showed presence of the elements: Na, Mg, Ca, K, Fe and these elements are included in the present investigation (see table 3). Some elements are a part of the clay minerals lattice e.g. magnesium and aluminum [Brady, 1984]. During firing some clay minerals partly are transformed into a glass matrix and some ions in the lattice are exchanged during firing [Cultrone et al., 2001].

Table 3. Water extractable cation concentrations in different brick types.

| Brick type | Ca [mole/kg] | Na [mole/kg] | K [mole/kg] | Mg [mole/kg] | Fe [mole/kg] | Sum of measured cations [mole/kg] | Sum of measured cations [mole/L]*** |
|----------------------------------|------------------------------------|------------------------------------|------------------------------------|-------------------------------------|---------------------|--|--|
| Falkenløwe Bright (triple) | 0.002016 +/- 3.6e ⁻⁵ | 0.001593 +/- 5.3e ⁻⁵ | 0.000372 +/- 1.5e ⁻⁴ | 0.000404 +/- 1.5 e ⁻⁵ | <1.1e ⁻⁵ | 0.00439 | 0.00175 |
| Falkenløwe Medium (triple) | 0.001239 +/- 2.0e ⁻⁵ | 0.000775 +/- 1.1e ⁻⁵ | 0.000189 +/- 1.4e ⁻⁴ | 0.000120 +/- 3.0e ⁻⁶ | <1.1e ⁻⁵ | 0.00233 | 0.00093 |
| Falkenløwe Dark (triple) | 0.001449 +/- 7.1e ⁻⁵ | 0.000710 +/- 5.3e ⁻⁵ | 0.000129 +/- 3.0e ⁻⁶ | 0.000091 +/- 4.3e ⁻⁶ | <1.1e ⁻⁵ | 0.00238 | 0.00095 |
| Wewers gul (triple) | 0.004439 +/- 2.8e ⁻⁴ | 0.001371 +/- 1.7e ⁻⁵ | 0.000349 +/- 1.5e ⁻⁵ | 0.000125 +/- 3.0e ⁻⁶ | <1.1e ⁻⁵ | 0.00629 | 0.00251 |
| Wewers rød (double) | 0.002595 +/- 4.5e ⁻⁷ | 0.001666 +/- 4.0e ⁻⁵ | 0.000568 +/- 2.7e ⁻⁶ | 0.000148 +/- 2.9e ⁻⁷ | <1.1e ⁻⁵ | 0.00498 | 0.00199 |
| Brarup Church 1300 AC** | - | 0.05 | 0.01 | - | * | 0.06 | × |

** from [Larsen 2007] – below detection limit 0.01 mole/kg * Not measured × not possible to convert

*** mole/L is calculated on basis of the added liquid for the measurements and used in section 4.3

4.2.1 Iron

Iron is present in the original clay matrix as Fe^{2+} or Fe^{3+} [Brady, 1984]. Since exchange of some ions in the lattice is known to occur during firing these could contribute to the amount of soluble ions, too. The mineral form iron(III)oxide (Fe_2O_3) is termed hematite. A correlation between hematite and firing temperature was found by [Schumann, 1997].

In clays with low lime content, the hematite amount is increasing with increasing firing temperature between 700 and 1210°C and this affects the color of the brick. The color intensity is dependent of the achieved firing temperature and is orange at low temperatures, red at higher temperatures and brown at the highest brick firing temperatures [Schumann, 1997]. This is supported by Cultrone et al. (2001) measurements, where a significant increase in hematite was measured at temperatures above 1000°C.

Schumann (1997) elaborated a method for subsequent measurement of the firing temperature for bricks with iron content above 3-4wt% and low calcium carbonate content (as in case of red bricks). This determination includes firing of brick samples at specific temperatures to find the correlation between temperature and hematite content measured by x-ray fluorescence analysis, to determination of a standard curve. The actual firing temperature is subsequently found by X-ray diffraction. This clearly illustrates the influence of hematite on the color of the brick.

Presence of calcium carbonate content in the brickwork mixture limits access of the iron oxide for hematite formation; the higher calcium carbonate content, the lower access of iron oxide. By presence of considerable amounts of calcium carbonate, calcium is build into Calcium-Aluminum-Silicates. The soluble content of Fe was measured to below the trustable area of the AAS ($< \frac{1}{2}$ of the smallest standard 0.500 ppm) and therefore not considered.

4.2.2 Other cations

Empirical investigations of firing of clay bricks by [Cultrone et al., 2001] showed that some K is replaced by Na in the clay brick at 700°C. Additional Fe, Mg and Ti replace some Al in the original clay mineral lattice. At 1100°C the K content in the silicate phase decreases, whereas the calcium and silicium content increases.

The Ca content in the bright colored Falkenløwe brick is significantly higher than in the medium and dark colored (table 3). However, Wewers yellow and Wewers red both have even higher contents.

Correspondingly, the Na content is highest in the bright colored brick and no significant difference was measured between medium and dark colored Falkenløwe bricks. The measured Na content for Wewers yellow, Wewers red and Falkenløwe bright are similar.

K is highest for the bright colored Falkenløwe brick whereas no significant difference is present between medium and dark colored Falkenløwe brick corresponding to [Cultrone et al., 2001] since replacement of K by Na in the silicate phase by a low brick firing temperature (700°C) must lead to increased amount of non lattice bound K which is soluble. The sodium content should according to this [Cultrone et al., 2001] decrease; however, since this does not occur sodium could also take part in other reactions. The K content is slightly higher for Wewers red, whereas Brarup Church possesses significant higher K content than for all the other brick types.

The bright colored Falkenløwe brick has approximately a factor 3 higher Mg content than all the other brick types which may suggest that the Mg content is dependent of the firing temperature.

The present measurements suggests that the Ca, Na, K and Mg content is dependent of the firing temperature since significant higher amounts were measured in Falkenløwe bright brick.

Differences in cation content between Falkenløwe (bright, medium and dark) and Wewers Yellow and Wewers yellow suggests differences in the rawmaterial.

The higher measured values for Brarup Church compared to all the other bricks regarding K and Na could indicate that ion accumulation had happened over the bricks 700 years lifetime.

4.3 Electrical conductivity

An overview of the soluble ions in a solution is given by the electrical conductivity (κ). All ions contribute to the conductivity, where the contribution from each type of ion depends on the specific ions charge and size. This method must be used with cautiousness as concentrations of different ions are not taken into account [Laidler et al., 2003], however, for an overview the conductivity measurement is useful. By use of the above measured cation concentrations (c_c , the sum of cations in mole/L) from section 4.2, conversion into the general comparable parameter molar conductivity was possible ($\Lambda = \kappa/c_c$). The results are listed in table 4.

Table 4. Electrical conductivity measurements.

| Brick type | κ [mS/cm] | Λ [cm ² ·S/mol] |
|-----------------------------------|---------------------|---------------------------------------|
| Falkenløwe Bright (five) | 0.32 +/- 0.04 | 184 |
| Falkenløwe Medium (five) | 0.18 +/- 0.01 | 198 |
| Falkenløwe Dark (five) | 0.18 +/- 0.03 | 192 |
| Æbleholt Bright (five) | 0.38 +/- 0.05 | - |
| Æbleholt Medium (triple) | 0.12 +/- 0.006 | - |
| Gl. Amtsvej 7 – red (triple) | 0.84 +/- 0.35 | - |
| Gl. Amtsvej 7 – yellow (triple) | 1.20 +/- 0.04 | - |
| Gl. Amtsvej 5 – A yellow (triple) | 0.25 +/- 0.01 | - |
| Gl. Amtsvej 5 – B yellow (triple) | 0.35 +/- 0.06 | - |
| Wewers yellow (five) | 0.53 +/- 0.03 | 211 |
| Wewers red (triple) | 0.32 +/- 0.02 | - |
| Egernsund (triple) | 0.28 +/- 0.01 | - |

- Anion content not measured which made calculation impossible

Comparing Falkenløwe bright and Æbleholt bright with Falkenløwe and Æbleholt medium and dark colored bricks there is a higher electrical conductivity for the bright bricks. This is in consistence with the sum of the measured anion and cation contents in section 4.1 and 4.2. Additional Falkenløwe and Æbleholt bricks electrical conductivities are within the same level for the different brick colors.

The new red bricks Wewers red and Egernsund red produced in a tunnel oven have electrical conductivities within the same area. Higher electrical conductivity was found for the new yellow bricks than for the new red bricks (comparison of Wewers yellow, Wewers red and Egernsund).

A significant difference between the bricks in construction (Gl. Amtsvej 7 red and yellow) and fully exposed bricks (Gl. Amtsvej 5 A and B) was found were an accumulation of ions seems to have occurred in construction whereas the weathered bricks had reduced ion content. The visual deteriorated brick Gl. Amtsvej 5 A had the lowest electrical conductivity indicating that the weathering is not due to chemical attack. No pronounced deviation differences within the multiple determinations were observed except in the case of Gl. Amtsvej 7 red. The results shown in table 4 indicate through the measurement of the electrical conductivity that the amount of soluble ions in the brick is dependent of several factors: firing conditions, raw material, exposure and exposure time.

Comparison of the contents of anions, cations and electrical conductivity reveals interesting connections. The electrical conductivity for Falkenløwe bright and Wewers yellow is in the same level (highest for Wewers yellow). This is also noticed regarding the total content of the measured cations. Contrary the total content of the measured anions were significantly lower in Wewers yellow and this suggest presence of a pronounced concentration of other anions than the measured. It is likely that this is because the carbonate in the yellow bricks is soluble to some extent.

By calculation of the molar conductivity based on the cation content the electrolyte concentrations were taken into account, and variation therefore suggest differences in ion charge where the higher molar conductivity values for Falkenløwe medium and Wewers yellow suggests presence of relative more ions or ions with higher valence than in the case of Falkenløwe bright and dark. This could be caused by substitution of some ions in the clay lattice as measured by [Cultrone et al., 2001]. This corresponds to the measured values in table 3. The amount of Ca and Na is minimum a magnitude higher than for the other ions and must for this reason be considered as dominating. And e.g. a decrease in Ca with the valence two by increasing firing temperatures with Na with the valence one could justify for changed molar conductivity.

Comparison of the sum of measured cations in table 3 and the electrical conductivity in table 4 shows good consistence and measurement of the electrical conductivity does for this reason seams to be a satisfying measure for the relative amount of total ions.

5. Influence of pH changes on the chemical composition and resistance against the pH changes

5.1 Acids influence on the ionic content

Masonry is influenced by rainwater, which due to presence of sulfuric acid (H_2SO_4) can have pH from 5.6 (natural pH of rainwater) down to pH 3. [Schumann, 1997]

The solubility of many compounds is pH dependent. Bricks fired at reduced atmosphere have black cores and their compounds of Al and Fe solubility increases at pH above 8 and below 9, respectively [Schumann, 1997].

The dependency of cations solubility related to pH was investigated by [Schumann, 1997] by submerging brick samples (fired by 900°C , 1040°C and 1150°C) into nitric acid (HNO_3) and sulfuric acid (10 wt% dissolution) until no further weight loss could be registered (250 days) and measure changes by X-ray diffraction.

Relative changes in the amount of Al, Ca, Mg, Fe, Na, K, Si and Ti was investigated. A general tendency was the connection in which the cations: Al, Ca, Mg, Fe, Na and K was dissolved in the acid. Calcium and sodium dissolved to the highest extend, however with a decreasing amount by increased firing temperature. The relative amount of Si increased whereas no significant changes were observed for Ti. The temperatures influence on the solubility was explained by a change in inner surface during the firing [Schumann, 1997], where the inner surface area decreases significantly by increasing firing temperatures.

[Schumann 1997] measured higher cations solubility in 10 wt% sulfuric acid (H_2SO_4) than 10 wt% nitric acid (HNO_3). Meanwhile it must be noticed that the H^+ concentration is slightly higher in 10% sulfuric acid (calculated $\text{pH} = -0.31$) than 10 wt% nitric acid (calculated $\text{pH} = -0.20$).

5.2 Resistance against pH changes

Some materials can possess buffer capacity against pH changes e.g. calcareous soils can buffer acidification [Ottosen et al., 2001].

In this section some bricks resistance against pH changes from acid and base is investigated.

The resistance of Wewers yellow against acidification was investigated by [Ottosen & Rørig-Dalgaard., 2007] and a buffering capacity was present, which to some extent could resist acid influence. The ability to resist acid influence is expected to be caused by the carbonate content which possess buffer capacity. Clay for red bricks originally contains 0-3 wt% carbonate and 17-25 wt% for yellow bricks [Rasmussen, 1992]. Even though firing transforms the calcite to burned lime (at temperatures above 830-900°C), differences in carbonate contents between red and yellow bricks were expected both due to different temperature induced brick colors and composition of the original clay. [Elert et al., 2003] reports detection of significant amounts of carbonates in many historic buildings. The carbonate content was measured for Falkenløwe bright, medium and dark colored brick and for Wewers yellow, table 5.

Table 5. Carbonate content for Falkenløwe bright, medium and dark and Wewers yellow.

| | Falkenløwe bright (triple) | Falkenløwe medium (triple) | Falkenløwe dark (triple) | Wewers yellow (double) |
|---------------------------|----------------------------|----------------------------|--------------------------|------------------------|
| CO ₃ [mole/kg] | 0.043 +/- 0.014 | 0.041 +/- 0.013 | 0.053 +/- 0.0004 | 0.05 |

The variation in acid soluble carbonate content was small and it is questionable whether the method is suitable for measurement of low contents.

Also influence from base can occur (e.g. from an electric DC field or in the border between cement mortar with high pH (above 13) and the brick) and resistance against base influence was investigated, too. Figure 5.

Both in figure 5 (a) and (b), dots showing pH in solution is covered by dots from measurements. Contrary to the yellow brick (Wewers) the red brick (Falkenløwe) did not possess significant resistance against acid influence under the chosen circumstances and these measurements dots cover dots showing pH in solution in figure 5 (a). This is supposed to be a general difference between yellow and red bricks which are attributed a higher carbonate content in the yellow brick even though this was not supported by the measured carbonate contents in table 5. Since a difference in buffer capacity was measured between the red Falkenløwe brick and the yellow brick Wewers, the absence of difference between the measured carbonate in table 5 is assumed to be caused to uncertainties of the measurement method in case of relatively small contents or other buffering systems.

The acid buffering capacity is found as identical amount (mole) of acid and buffer material used to neutralize the acid [Grimshaw & Harland, 1975]. In this case it is most probably that the buffering occurs by decomposition of carbonate in the yellow brick. By ongoing acid influence all present carbonate will eventually be consumed which ends the carbonates buffer capacity here seen by increasing concentrations and agitation duration. Meanwhile other buffer systems could also be present.

Neither the yellow brick “Wewers” nor the red brick “Falkenløwe” had a significant resistance against base independent on base concentration and agitation duration and the measurements dot and dot showing pH in solution are all covering each other.

In case of the red Falkenløwe brick no significant buffer capacity was measured independent of concentration and agitation duration, which suggests that a change in the chemical composition of these bricks is less likely. However, a pH change occurs presumably faster in Falkenløwe red than in Wewers yellow during acidification.

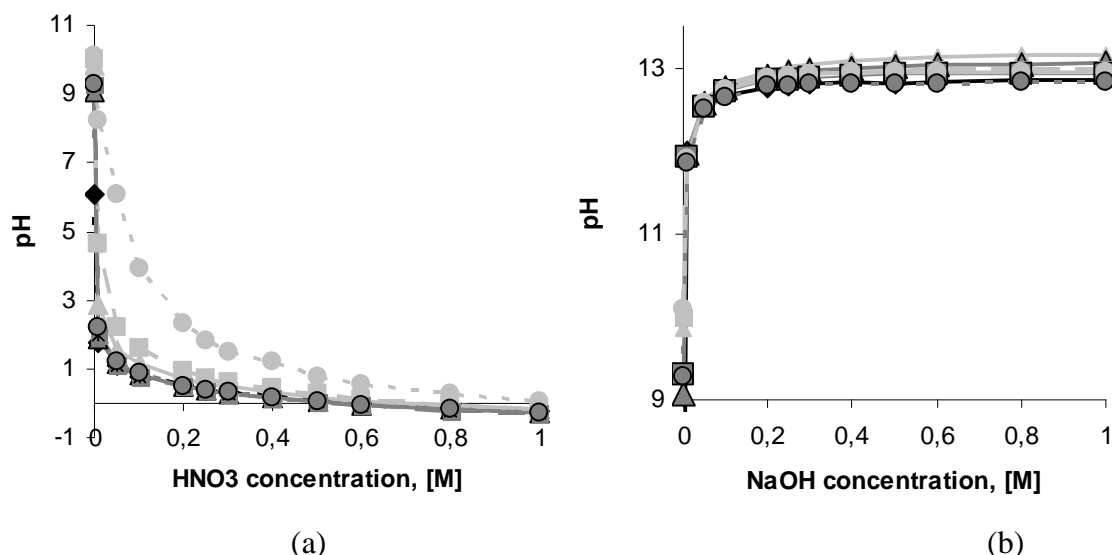


Figure 5. (a) Acid resistance and (b) alkali resistance. pH in \blacklozenge solution. Falkenløwe medium agitation time \blacktriangle 1 hour \blacksquare 5 hours \bullet 24 hours. Wewers yellow agitation time \blacktriangle 1 hour \blacksquare 5 hours \bullet 24 hours.

5.3 pH measurements

Environmental influence on existing bricks by acidic rain is presumably followed by pH changes. The pH is expected to decrease as a function of exposure. pH measurements for all the bricks are listed in table 6.

Table 6. pH values for different brick types.

| Brick type | pH |
|-----------------------------------|---------------|
| Falkenløwe Bright (five) | 9.1 +/- 0.03 |
| Falkenløwe Medium (five) | 9.2 +/- 0.08 |
| Falkenløwe Dark (five) | 9.4 +/- 0.03 |
| Æbleholt Bright (double) | 8.0 +/- 0.07 |
| Æbleholt Medium (triple) | 9.3 +/- 0.02 |
| Gl. Amtsvej 7 red (triple) | 9.1 +/- 0.14 |
| Wewers red (triple) | 9.3 +/- 0.02 |
| Egersund red (triple) | 9.3 +/- 0.03 |
| Gl. Amtsvej 5 yellow- A (triple) | 8.8 +/- 0.04 |
| Gl. Amtsvej 5 yellow - B (triple) | 8.2 +/- 0.15 |
| Gl. Amtsvej 7 yellow (triple) | 9.3 +/- 0.05 |
| Wewers yellow (five) | 10.4 +/- 0.03 |

There seems to be a tendency for higher pH in new yellow bricks (Wewers yellow) than new red bricks (Wewers red, Egersund red) which is ascribed to higher calcium carbonate content. This tendency could directly be seen between the two new bricks:

Wewers yellow and Wewers Red and between the two 100 years old bricks: Gl. Amtsvej 7 Red and Gl. Amtsvej 7 Yellow.

Both in Æbleholt and Falkenløwe a pH decrease is measured for the darker colors than for the brighter colors which is in good consistence with Schumann (1997) which described that fewer surfaces can be influenced by higher firing temperatures. [Elert et al., 2003] describes that firing temperatures above 1100°C for calcareous clay and 1000°C for non-calcareous clay is required to produce bricks durable to resist laboratory weathering tests.

By comparison of Falkenløwe, Æbleholt and Gl. Amtsvej 7 there seem to be a tendency for lower pH in the bricks with the highest environmental exposure. Most distinct is the environmental influence on Gl. Amtsvej 5 A and B which despite of the yellow color has a remarkably low pH.

In consistence with the expectations the new bricks produced in a tunnel oven (Wewers red, Wewers yellow, Egernsund) shows lower deviation than the new brick produced in a circular kiln (Falkenløwe bright, medium and dark).

6. Conclusion

The environmental effect and the colors influence on the amount of soluble ions were investigated for a variety of new and old, yellow and red bricks.

The standard DIN 38 414 (S4) elaborated for examination of water, waste water and sludge was tested for preparation of pH and ion content measurements in bricks and found to result in satisfying, robust measurements..

Measurement of the soluble anion content, cation content and electrical conductivity related to the chemical changes described in the literature suggest that the reason for the different colors in Falkenløwe bricks are related to variation in firing temperature. Mainly the description of increased color intensity as a consequence of increased hematite formation by increasing temperature and the higher sulfate content in the bright bricks supported the hypothesis. Significant higher ion content was found for the bright colored Falkenløwe brick compared to the medium and dark colored brick suggesting lower glass matrix formation in the bright brick. Both traditional firing methods (circular kiln, tunnel oven) and clay mixture was found to have significant influence on the amount of soluble ions.

Falkenløwe and Wewers yellow showed no significant ability to resist acid or alkaline exposure respectively under the chosen circumstances and changes due to environmental influence is therefore expected to initiate from the beginning of exposure.

The environmental effect was found to have major influence on both the amount of soluble ions and the pH since pH decreased approximately from 10 to 8 by extensive weathering and the electrical conductivity increased approximately up to a factor 4 when placed in this specific building.

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Diffusion and electromigration in clay bricks – influenced of the firing induced differences in the pore system

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Abstract

Ion transport in porous materials has been studied for decades. However, the interaction between the pores and the overall pore system aggravate to obtain a clear picture and predict diffusion and electromigration (transport in an applied electric field). Examination of specific bricks and the shape, size and interconnection of the pores was carried out. In the present paper the pores were studied at a microscopic level, the interconnected pore system at a macroscopic level and compared with the measurement of the corresponding ion transport to contribute to an overall understanding of ion transport in porous materials.

The pore structure and pore system in bricks are influenced by the firing degree, clay mixture composition and ion content. In the present paper the pore structure and the pore system were in focus by neglecting effects from clay mixture composition and ion content by using the same brick type from the same brickwork (delivered at the same pallet). The used bricks were fired in a circular kiln where uneven heating during firing occurs. Significant color differences were visible between the bricks in the pallet and for the investigation purpose they were divided into the groups: bright, medium and dark colored bricks. This increasing color intensity is most probably caused by increasing firing temperatures.

The three groups of bricks were investigated for saturation coefficient, open porosity, dry density and water absorption coefficient and clarified differences. The pore system was studied in thin sections and showed by increasing brick firing temperatures a change from relatively many tiny pores to fewer bigger pores. Also significant difference in the pore system as a function of distance to the surface was found for all the three brick types.

Influence of the pore structure on ion transport through the water saturated pore system of the bricks was found likely by resistance measurements and an increasing resistance

was found for increasing brick firing temperatures. The effective diffusion coefficient was empirical determined for chloride and sodium by application of an electric DC field across whole bricks. The lowest effective diffusion coefficient was found for the dark colored brick, increasing for the medium and bright colored respectively. This suggests that in clay bricks many small pores favors ion transport in relation to fewer thicker pores.

Keywords

Clay bricks, color variation, saturation coefficient, open porosity, density, water absorption coefficient, thin section, resistance, effective Cl diffusion coefficient, effective Na diffusion coefficient

1. Introduction

Salt induced deterioration is problematic both in recent structures and in historic structures where a longer exposure period can intensify the contamination. In order to predict the movement of water and ions in structures empirical investigations and simulation tools are used at present e.g. RUNSALT, DELPHIN 5.

Ion transport, as diffusion, convection or electromigration in porous materials is dependent on the pore size and pore system. Therefore ion transport in a porous material must be described by the actual measured ion transport in the specific material. The porosity and structure was by [Buchwald & Goretzki, 1996], [Buchwald & Kaps, 1999B], [Terheiden & Kaps 2003] used to describe the material dependent ion diffusion and [Cultrone et al., 2001], [Elert et al., 2003], [Nijland & Larbi, 2004] recognized the firing degree influence on the pore structure in bricks and thus the firing degree is indirectly influencing ionic transport.

Calculation of chloride transport induced by a concentration gradient (diffusion) is by Castellote et al. (1999) described as common practice in relation to concrete and used for assessment of the resistance of the concrete to the transport of chloride. However, as the evaluation of ion diffusion in water saturated species from diffusion tests is extremely slow, the application of an electrical field, which accelerates ionic transport, could reduce the testing time. This was shown possible at low chloride concentrations in concrete where all chlorides remain free in the pore solution [Castellote et al., 1999].

The pore structure and pore system in bricks are influenced by the firing degree, clay mixture composition and ion content. Modern produced bricks are fired in a tunnel oven with an even temperature distribution resulting in approximately the same brick firing degree. Differences in the pore system in newly produced bricks from a tunnel oven will therefore predominantly appear in case of different compositions of the clay mixture. In the present paper the differences in pore structure and pore system induced by differences in the firing degree is in focus. New uncontaminated bricks from the same pallet made by Falkenløwe were used to neglect the effect from: clay mixture composition and ion content. The Falkenløwe bricks were fired in a circular kiln with uneven heat distribution, resulting in varying firing degree of the bricks. The firing degree varied from low to high in relation to traditional brick firing degrees. This type

of bricks is made for restoration purposes. By choosing bricks from the same pallet (200 bricks), the major variation was most properly the firing temperature.

In the present paper changes induced by the firing degree on the pores and their interconnected system is investigated in relation to ion transport across the bricks. The differences between the poor, traditional and hard fired bricks are presented macroscopic by capillary saturation, open porosity, dry density and water absorption coefficient and microscopic by thin sections and its influence on the ion transport by electric resistance measurements across the bricks and by effective diffusion measurements.

2. Materials and methods

2.1 Materials

Bricks from Falkenløwe [www1] (termed Munkesten) were used. The name Munkesten is related to its size which is the old traditional Danish brick size (approximately 28 cm × 7 cm × 14 cm). These bricks are made for restoration purpose of older historic building. They are handcrafted and burned in a circular kiln as in ancient time. Comparing investigations have shown similar properties (regarding pore size distribution and porosity) between original Danish medieval bricks and Falkenløwe bricks [Larsen, 1996]. In a circular kiln the bricks are fired at varying firing temperatures dependent on the actual position of the bricks in the kiln in relation to the heating source. The bricks with the most distinct color variation were chosen for the investigation, figure 1. In Rørig-Dalgaard & Ottosen (2008) the water soluble ionic content of Falkenløwe bricks was measured for the bright, medium and dark colored bricks shown in figure 1. The difference in water soluble ionic content for the different brick colors was compared with other investigations of changes in the water soluble ionic content made on clay mixtures fired at varying temperatures. On this basis it was likely, that the increasing color intensity was caused by increasing firing temperatures.



Figure 1. The dark, medium and bright colored bricks.

2.2 Methods

The water saturation coefficient was found by submerging the bricks into a solution consisting of 79.61 mg NaCl/L in distilled water for 3 days and calculated as weight gain in percentage. The water content was found after drying of the brick samples at 105°C until equilibrium (one day) and calculated as weight loss.

The open porosity was found by vacuum saturation of the dry bricks and subsequently calculated as the relationship between water gain with vacuum saturation and oven dry and divided with the weight difference of the bricks weighed above and below water.

The dry density was found by dividing the oven dried mass with the weight difference of the vacuum saturated brick measured above and below water in relation to the density of water at the actual temperature.

The water absorption coefficient was found by weighing the water uptake as a function of time until no further water uptake was measurable (equilibrium). The water absorption coefficient was determined as the slope coefficient of the water uptake as a function of the square root of the time [ISO/FDIS 2002].

Thin sections were prepared from 1 cm × 3 cm × 5 cm pieces from the bricks, destructively cut out of the material. The pieces were taken from the borders of a bright, a medium and a dark colored brick. The dry brick samples were impregnated with a yellow fluorescent resin and polished until a thickness of approximately 25µm was reached. The final cross sections of the thin sections were approximately size (2.5 cm × 4.8 cm) The impregnation with the (yellow) fluorescent resin results in the air voids (pores) becoming more visible in blue light (wavelength: 450-495 nm) as green spots or areas.

2.2.1 Procedure for contaminating the bricks with salt

The bricks were submerged in a solution of 79.61 mg NaCl/L in distilled water for 3 days. The aim was to obtain a chloride concentration of 1.0 wt% chloride in the brick as this concentration is problematic and realistic in relation to salt induced decay. After the 3 days submersion, the bricks were carefully wrapped in plastic film to minimize evaporation.

2.2.2 Setup

The electric resistance and effective diffusion coefficient investigations were made with whole bricks in order to minimize the source of errors originating from the edges and obtain general results in case of variations throughout the bricks. In the electrokinetic salt removal experiments the electrical DC field was applied with two electrode units. They were placed on the long, narrow side of the brick in two holes that were cut in the plastic film, see figure 2. The electrode units each had an area of 5.5 cm × 7.0 cm and a special clay poultice was applied between the brick surface and the two metallic electrodes. Flexible plastic forms were placed around the poultice to ensure the same amount of poultice in all the experiments. The forms had a height of 1.7 cm which corresponds to the height of the poultice between metallic electrodes and brick.

To obtain an effective desalination, a newly developed poultice was used. The poultice consisted of kaolinite clay, buffer component and distilled water and is described in details in Rörig-Dalgaard & Ottosen (2008 C) with the possibility to obtain a high desalination effect.



Figure 2. Laboratory setup where the poultice with electrodes is placed on the long, narrow side of the brick.

2.2.3 Experimental overview

All the experiments were carried out with capillary saturated bricks and an initial chloride content of approximately 1.0 wt %. In the experiments with constant current 80 mA was applied (section 4.3) corresponding to 2.1 mA/cm² electrode and in the experiments with constant potential drop 10 V was applied (section 4.4) corresponding to 44.4 V/m between the electrodes.

Table 1. Experimental overview.

| | Color | Duration [hours] | Voltage drop [V] | Current [mA] |
|--------|--------------|-----------------------------|-----------------------------|-------------------------|
| B.R 1 | Bright | 24 | 25.6→8.1 | 80 |
| B.R 2 | Bright | 24 | 27.8→8.7 | 80 |
| M.R 1 | Medium | 24 | 28.4→11.2 | 80 |
| M.R 2 | Medium | 24 | 28.7→7.9 | 80 |
| M.R 3 | Medium | 24 | 33.5→9.9 | 80 |
| M.R 4 | Medium | 24 | 37.9→9.1 | 80 |
| M.R 5 | Medium | 24 | 26.9→9.6 | 80 |
| M.R 6 | Medium | 24 | 30.2→10.2 | 80 |
| M.R 7 | Medium | 24 | 30.0→13.0 | 80 |
| M.R 8 | Medium | 24 | 28.8→8.4 | 80 |
| M.R 9 | Medium | 24 | 28.7→8.6 | 80 |
| M.R 10 | Medium | 24 | 30.1→9.1 | 80 |
| D.R 1 | Dark | 24 | 33.5→11.2 | 80 |
| D.R 2 | Dark | 24 | 28.0→9.5 | 80 |
| | | | | |
| B 1 | Bright | 0-24* | 10 | 57→127 |
| B 2 | Bright | 24-48** | 10 | 40→102 |
| M 1 | Medium | 0-24* | 10 | 47→115 |
| M 2 | Medium | 24-48** | 10 | 38→87 |
| D 1 | Dark | 0-24* | 10 | 42→89 |
| D 2 | Dark | 24-48** | 10 | 31→71 |

* The result is evaluated on the salt extraction measured between 0 to 24 hours experimental duration.

** The results are evaluated on salt extraction measured between 24 to 48 hours experimental duration.

3. Ion transport in a porous material

3.1 Diffusion

Concentration gradient induced transport in a free liquid is termed, diffusion and the diffusive flux is defined in Fick's first law as [Laidler et al., 2003]:

$$J = -DA \frac{\partial c}{\partial x} \quad (\text{I})$$

Where D is the diffusion coefficient, A the area through which the ions cross and $\partial c / \partial x$ is the concentration gradient of the solute.

3.2 The influence of the pore system on ion transport

Ion transport equations for liquids cannot be used directly in porous materials since ion transport in a porous material is dependent on the pore distribution, structure and size, as well as the saturation degree [Buchwald & Goretzki, 1997], [Vogt & Kriegel, 2005], [Buchwald & Kaps, 2000] and the electrolyte concentration [Truc et al., 2000].

Buchwald & Goretzki (1997) found the free diffusion 0.1 M NaCl, 0.5 M NaCl and 0.6 M Na₂SO₄ in a liquid to be approximately a factor 10⁵ higher than in the pores of a water saturated brick. However, the relative diffusion velocity for different ions in the brick was consistent with the order found for free diffusion in a solution.

Toumi et al. (2007) estimated the effective diffusion coefficient for chloride and sodium to be 27 and 55 times faster in a bricks than in concrete. In cement paste the effective diffusion coefficient in general is also a function of age since it is affected of the pastes hydration degree and water/cement ratio [Geiker et al., 2007] and chloride binding [Castelotte et al., 1999] as it is a chemical reactive material.

Actual measured ion transport in a porous material under steady-state conditions is termed effective diffusion. Truc et al. (2000) suggested a material dependent link between traditional diffusion (D₀) in a free solution and the effective diffusion (D_e) in a porous material:

$$D_{\text{eff}} = p \frac{\delta}{\tau} D_0 \quad (\text{II})$$

Where p is the porosity, τ is the tortuosity (the increase in effective diffusion road) and δ the constrictivity (the resistance on the ion transport from narrow pores determined on the proportion between ion and pore diameter, always below 1).

Buchwald & Kaps (1999 B) found no coherence between ion transport and the pore size in bricks, mortar and sandstones. However, they found that the diffusion coefficient is inverse proportional with the tortuosity in consistence with equation II. They concluded that the interconnected pore structure throughout the pore system was the determining factor for the diffusion coefficient.

Even though equation (I) and (II) were derived for diffusion in a free solution the influence of the pore structure on transport in an electric field can be expected similar.

3.3 Electromigration

When applying an electric DC field across a moist, porous material, the ions in the pore water will be attracted towards the electrodes and initiate an ion transport, a phenomenon termed electromigration. Electromigration [$\text{m}^2 \cdot \text{s}^{-1}$] in a free electrolyte is in Laidler et al. (2003) described as:

$$D_0 = \frac{k_B \cdot T \cdot u \cdot L}{F \cdot |z|} \quad (\text{III})$$

Where k_B is the Boltzmanns constant ($1.3807 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$), T the temperature (K), u is the ionic mobility ($\text{m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$), L is Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$), F is Faradays constant ($96485 \text{ C} \cdot \text{mol}^{-1}$) and $|z|$ is the unit charge of the ion. Andrade (1993) deduced an experimental expression for electromigration under steady-state conditions in cement, a so-called effective diffusion coefficient [$\text{m}^2 \cdot \text{s}^{-1}$]:

$$D_{\text{eff}} = \frac{J \cdot R \cdot T \cdot l}{z_j \cdot F \cdot c_j \cdot \Delta E} \quad (\text{IV})$$

Where J is the diffusing flux ($\text{mol} \cdot \text{s}^{-1}$), R the gas constant ($8.3143 \text{ J mol}^{-1} \cdot \text{K}^{-1}$), T the temperature (K), l is the distance between the electrodes (m), z_j is the electric charge of the species j , F is Faradays constant, c_j the ionic concentration of the species j ($\text{mol} \cdot \text{m}^{-3}$) and ΔE is the applied electric field (V).

The coherence between electromigration in cement under steady-state conditions (the so-called effective diffusion coefficient (D_{eff})) and under non-steady-state conditions (the so-called apparent diffusion coefficient (D_{app})) is in Castellote et al. (1999) described as:

$$D_{\text{app}} = \frac{D_{\text{eff}}}{p} \quad (\text{V})$$

Where p is the porosity of the material.

Dependent on the specific ions preference for transport, ion transport will proceed in a certain order. Ions with the highest ionic mobility will be preferred and transported first and the order is related to the size of the ions [Buchwald & Goretzki, 1996], table 3.

Table 2. Ionic mobilities for relevant ions [$\text{u}/10^{-8} \text{m}^2 \text{s}^{-1} \text{V}^{-1}$]

| | Cl^- | $\frac{1}{2} \text{NO}_3^-$ | $\frac{1}{2} \text{SO}_4^{2-}$ | $\frac{1}{2} \text{CO}_3^{2-}$ | K^+ | Na^+ | $\frac{1}{2} \text{Ca}^{2+}$ | $\frac{1}{2} \text{Mg}^{2+}$ |
|----------------|---------------|-----------------------------|--------------------------------|--------------------------------|--------------|---------------|------------------------------|------------------------------|
| Ionic mobility | 7.91 | 5.49 | 4.15 | 3.73 | 7.62 | 5.19 | 3.09 | 2.75 |

[Atkins, 1994] and [www2]

Consistence between theoretical ionic mobility in free solutions [Atkins, 1994] and empirical obtained results in porous materials has been shown by Ottosen & Rörig-Dalgaard (2008), Fajardo et al. (2006) and Ali et al. (1992) since increased ion transport was observed for ions with the highest theoretical ionic mobility. Ottosen & Rörig-Dalgaard (2008) observed that K^+ ions move faster than Na^+ ions in bricks in an applied electric field. Fajardo et al. (2006) and Ali et al. (1992) observed that K^+ ions moves faster than Na^+ , Mg^{2+} and Ca^{2+} in concrete under influence of an electric field.

4. Results and Discussion

4.1 The overall macrostructure

The focus of the material characterization in the present work is on material parameters related to whole bricks in order to minimize the source of errors originating from the edges and to obtain general results in case of variations throughout the bricks.

The saturation coefficient, open porosity, dry density, and water absorption coefficient were found in order to describe the interconnected pore system as a whole, table 4.

Table 3. Macroscopic material parameters.

| Brick color | Saturation coefficient* [wt%] | Open porosity [vol.-%] | Dry Density [$kg \cdot m^{-3}$] | Water absorption coefficient [$kg \cdot m^{-2} \cdot s^{-1/2}$] |
|-------------|-------------------------------|------------------------|-----------------------------------|---|
| Bright | 12.9 +/- 0.0 | 34.9 | 1750 | 0.23 |
| Medium | 12.6 +/- 0.4 | 33.0 | 1788 | 0.30 |
| Dark | 9.8 +/- 1.8 | 31.4 | 1801 | 0.32 |

* The saturation coefficients are average values from all the bricks listed in table 1.

The open porosity was highest for the bright colored brick (34.9 vol.-%), decreasing for the medium colored brick (33.0 vol.-%) and lowest for the dark colored brick (31.4 vol.-%). Elert et al. (2003) also found decreasing open porosity in bricks by increasing firing temperature, both for calcareous and non calcareous bricks investigated as a function of the firing temperature in the range 700°C - 1100°C.

The saturation coefficients showed a decreasing tendency for increasing color intensity. Bright: 12.9 wt%, medium: 12.6 wt% and dark: 9.8 wt% where the dark colored brick had a pronounced lower saturation coefficient than the bright and medium colored bricks. This is in consistency with Elert et al. (2003) where increasing saturation coefficient were reported by increasing firing temperatures up to 1000°C and 800°C for calcareous and non calcareous bricks respectively whereas the saturation coefficient decreased at higher firing temperatures.

The increasing density by increasing color intensity indicates a more compact material and thereby a higher vitrification degree (higher degree of particle interlocking) in consistence with the findings in Cultrone et al. (2001).

The water absorption coefficient is a measure for the absorption velocity. A high water absorption coefficient results in fast absorption and indicates a coarse grained material, contrary a small water absorption coefficient result in slow absorption and indicates a

fine grained material. A significant smaller water absorption coefficient was found for the bright colored brick than for the medium+dark colored brick indicating that the bright colored brick has a pore system with smaller pores compared to the medium and dark colored brick.

An additional investigation of segmented bricks was made. Slices of the bricks were made both horizontally and vertically. This segmentation was carried out to investigate differences in the pore structure throughout the brick. The results of water absorption coefficient from the vertical slices are shown in figure 3. However, it must be noted that the capillary rising height only was 3.5 cm for these slices and therefore was it only possible to measure for approximately 100 seconds before the brick piece were water saturated.

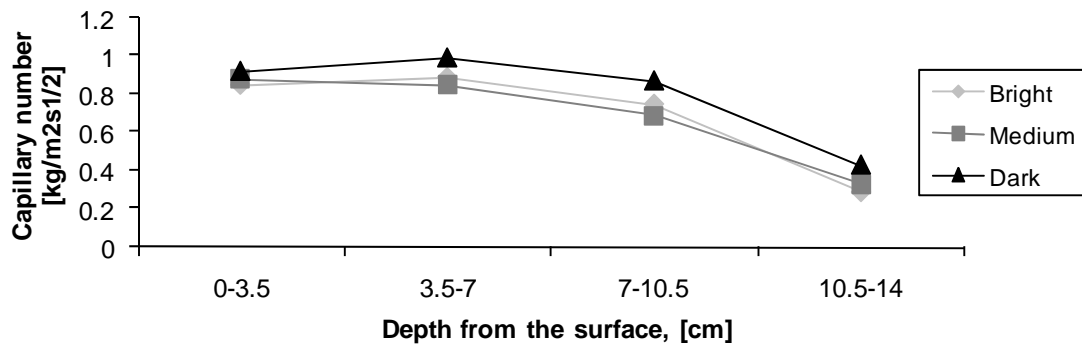


Figure 3. Water absorption coefficient of bricks as function of distance from the outer surface. The last measurement correspond to the center of the brick.

The results must therefore be considered as an identification of tendencies. A difference in the water absorption coefficient from the edge to the middle of the brick was in the order of a factor 2-3. This suggests a rather complex pore system with changing pore structure throughout the brick. The results also suggest that the dark colored brick has a coarser structure than the bright and medium colored brick.

4.2 The pore system

The sintering process in the clay mixture during firing changes the original material gradually [Schumann, 1997] and provided different firing temperatures is the reason for the color variation between the bright, medium and dark colored bricks, there must be a significant difference in the pore structure.

Examination of the samples in Polarized Fluorescent Microscope (PFM) impregnated with (yellow) fluorescent resin was used to obtain an overview of the pore structure in a cross section including: pore size, shapes and interconnections. One bright, one medium and one dark cross section was examined in PFM both along the border of the cross section (figure 4) and in the middle of the cross section (figure 5) and representative areas were chosen to the figures.

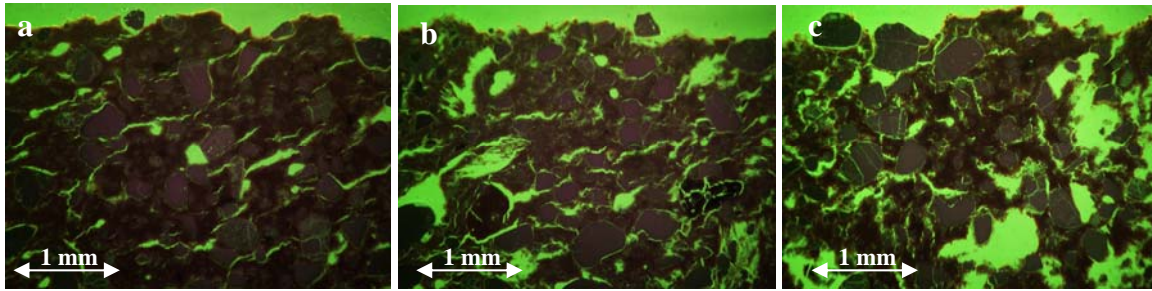


Figure 4. PFM pictures from the border of the cross section where the border is at the top of the picture (a) The bright colored brick (b) The medium colored brick and (c) The dark colored brick.

Close to the edge, the bright colored brick showed relative thin pores, the medium colored relative bigger pores and in the cross section of the dark colored brick the biggest pores were seen. There seems to be a tendency for pores with an increasing radius and areas with increasing color intensity and this is in good consistence with the measured values in table 3. Elert et al. (2003) also observed a change from smaller to larger pores at increasing firing temperatures, as a result of melting and coalescence of particles. Cultrone et al. (2001) observed a change from ellipsoidal to spherical pores during firing.

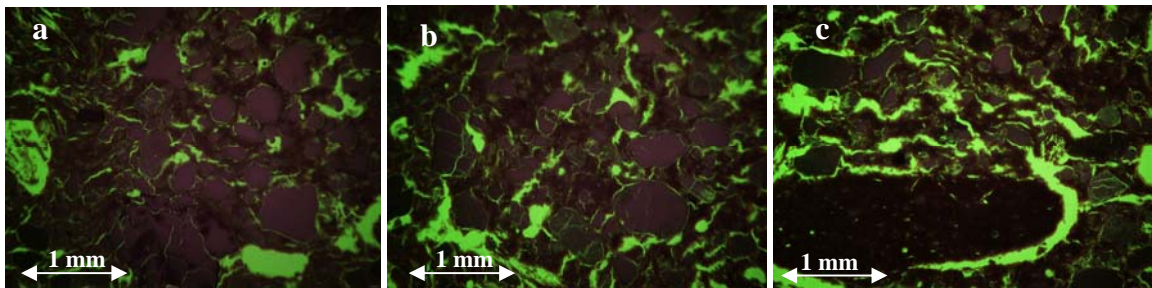


Figure 5. PFM pictures from the middle of the cross section. (a) The bright colored brick (b) The medium colored brick (c) The dark colored brick.

In the cross sections from the middle of the brick (figure 5), both small thin pores and areas with bigger pores were seen in the bright colored brick. Relatively thicker pores were observed with a higher degree of interconnection of the wider pores. In the cross section of the dark colored brick an even higher amount of thicker pores with a higher degree of connection between the wider pores was seen. For the dark colored brick the pore system seems oriented. In these cross sections, an increasing interconnection of the wider pore system seems to occur with increasing color intensity. In Addition there seems to be a tendency for parallel pores especially pronounced in figure 5 (c). Cultrone et al. (2001), Nijland & Larbi (2004) observed similar tendencies and suggested that this orientation also was present before firing and caused by compression during molding. Comparing the macroscopic parameters (table 3) with the observations from the PFM (figure 4 and 5) and with the results from Cultrone et al. (2001), Elert et al. (2003), Nijland & Larbi (2004), Rörig-Dalgaard & Ottosen (2008) it seems likely that the color variations of the investigated bricks were due to firing at different temperatures. Increasing firing temperatures caused increasing color intensity. The thin sections showed significant differences in the pore system and these differences influences the ion transport, which is shown in the following.

4.3 Contamination of the bricks with salt related to brick color

By choosing capillary saturated bricks, the influence of the water content on the electrical resistance across the brick was relative smaller compared to bricks with lower water content since the electrical resistance decrease almost exponential with increasing water contents [Rörig-Dalgaard, 2002].

The actually obtained water, sodium and chloride contents are listed in table 4.

Table 4. Water, sodium and chloride content after pretreatment shown as an average of nine taken samples from each brick. The values are from three capillary saturated reference bricks: one bright, one medium and one dark brick.

| Brick type | Water content [wt%] | Na ⁺ [wt%] | Cl ⁻ [wt%] |
|------------|---------------------|-----------------------|-----------------------|
| Bright | 11.5 +/- 1.0 | 0.70 +/- 0.06 | 1.04 +/- 0.09 |
| Medium | 11.0 +/- 1.2 | 0.75 +/- 0.06 | 1.01 +/- 0.11 |
| Dark | 10.8 +/- 0.8 | 0.64 +/- 0.03 | 0.94 +/- 0.04 |

The tendency showed lowest: water, sodium and chloride contents for the dark colored brick increasing for medium and bright colored bricks. The 7 % difference between the highest (bright colored brick) and lowest water content (dark colored brick) resulted in approximately the same difference between the highest and lowest chloride and sodium contents respectively. Such variations in both water and ion contents should also be expected in existing constructions.

The initial ion concentrations in Falkenløwe bricks were measured for the bright, medium and colored brick [Rörig-Dalgaard & Ottosen, 2008] and was found to be marginal compared to the added NaCl contaminant (chloride ~ 0.0012 wt% and sodium ~ 0.0016-0.0037 wt%).

4.4 The influence of the pore system on the electric resistance

In order to estimate the influence of the pore systems on the ion transport, the impede of the pore system on the ion transport was described through the electrical resistance measurements across bricks. The electrical resistance was determined as a function of the pore structure of the bricks (defined from the brick color intensity). The experiments were carried out by applying a constant DC current of 80 mA across 2 bright colored bricks, 10 medium colored bricks and 2 dark colored bricks (see table 1). The total resistance across the brick was calculated from the initial measurements ($R = U/I$) and at the time where the lowest resistance occurred (with this setup after 24 hours duration for all the experiments), figure 6.

By application of the electric DC field desalination occurs in Falkenløwe bricks at chloride contents above 0.01 wt% [Rörig-Dalgaard & Ottosen, 2008 D] and therefore also in the present experiment with an initial chloride content of 1.0 wt%. During this desalination the ionic concentration within the pores decreases. The resistance across the moist and salt contaminated brick is a function of moisture and especially ion content. Thus the resistivity measurements were only made during the initial period in order to limit the influence of the ongoing desalination.

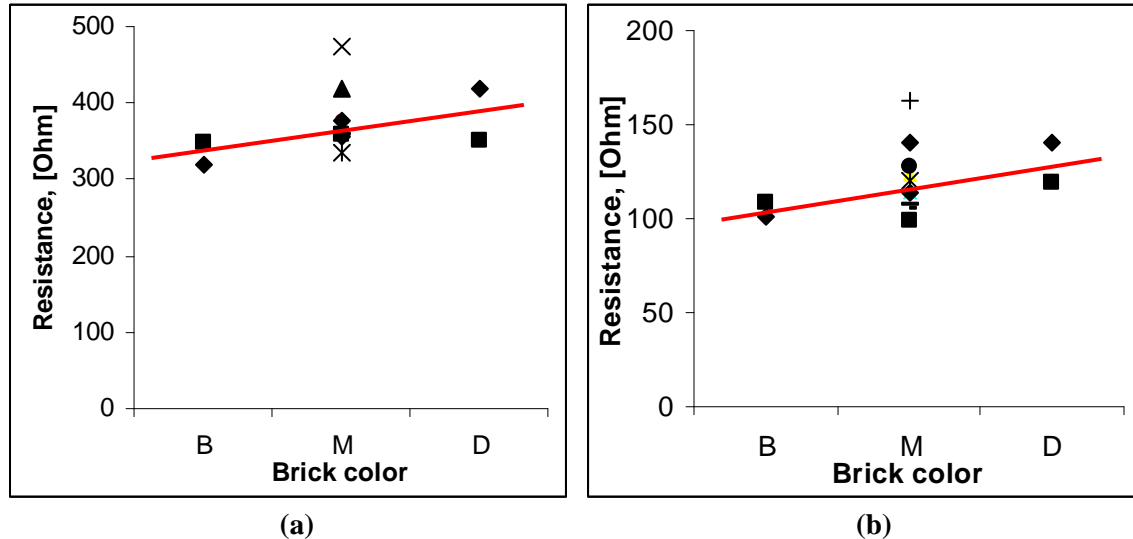


Figure 6. The initial resistance across the setup (a) and the resistance after 24 hours duration (b) as a function of the colors: bright (B), medium (M) and dark (D) colored bricks. Each dot represents a measurement of the total resistance across the setup and the solid lines show tendencies.

The resistance calculated from the initial voltage drop is not affected by varying ion and water reduction as happens during the treatment. For this reason the initial resistance is considered as the most material representative measurement. However, an increased resistance has been noticed by several authors at the beginning of experiments due to a reduced contact between electrodes, accumulation material and the underlying material, decreasing after establishment of good contact to the substrate [Lu et al., 2006], [Ottosen & Rørig-Dalgaard, 2007]. For this reason the resistance is also given at the time where the lowest resistance was measured (namely after 24 hours) since a good contact must have been obtained at this point, and at the same time the change from the initial ion and water contents is supposed relatively small. Both when the highest ($t=0$ hours) and lowest ($t=24$ hours) resistance was found the same pattern was seen. The electrical resistances were therefore evaluated after 24 hours. The highest resistance was found for the dark colored brick ($R_{24 \text{ hours}} = 129 \pm 15 \Omega$) decreasing for the medium colored brick ($R_{24 \text{ hours}} = 121 \pm 18 \Omega$) and lowest for the bright colored brick ($R_{24 \text{ hours}} = 105 \pm 5 \Omega$).

This increased resistance from the bright to the dark colored brick is supposed caused by the differences in pore structure. The pore structure investigated through thin sections (section 4.2) showed a change from many relative small pores to fewer wider pores with increasing firing temperature. Taking the impede of the pore structure on the ion transport in equation (II) into account, it suggests that an extension of the road (high tortuosity) of each ion through the brick causes the increased resistance for the ions across the bricks. This is a consequence of reduced numbers of pores (higher firing temperatures).

The present resistances were calculated for capillary saturated bricks with 1.0 wt% chloride (added as NaCl) and the electric resistance across the brick was highly influenced by the high water and ionic content. In case of lower water and ionic contents, the influence of the pore structures on the electric resistance is supposed to be higher.

4.5 The effective diffusion coefficients of Sodium and Chloride

The diffusion coefficients were found to describe the influence on the ion transport from the pore system.

By absence of competing ions the current will solely be carried by the ion in focus and thereby give the clearest picture of the influence of the pore structures on the ion transport through the bricks. Therefore ions with high ionic mobility were chosen: chloride and sodium. Chloride has the highest ionic mobility among the typical anions of contaminating building salts (table 2). Sodium also has a relatively high ionic mobility and of the relevant cations only potassium has a higher.

The experiments were carried out with bright, medium and dark colored bricks and these experiments were evaluated on basis of the extracted sodium and chloride contents in the poultices after 24 and 48 hours. In this time frame the changes in water and ion content is expected to be minor and a steady-state system was presumed. Therefore the calculated ion transport is termed effective diffusion coefficient according to the definitions in section 3.

When applying a constant voltage of 10 V, the varying resistances across the bricks results in varying current strengths. A comparison of the extracted ions shows a pattern for the pore structures impede on the ion transport.

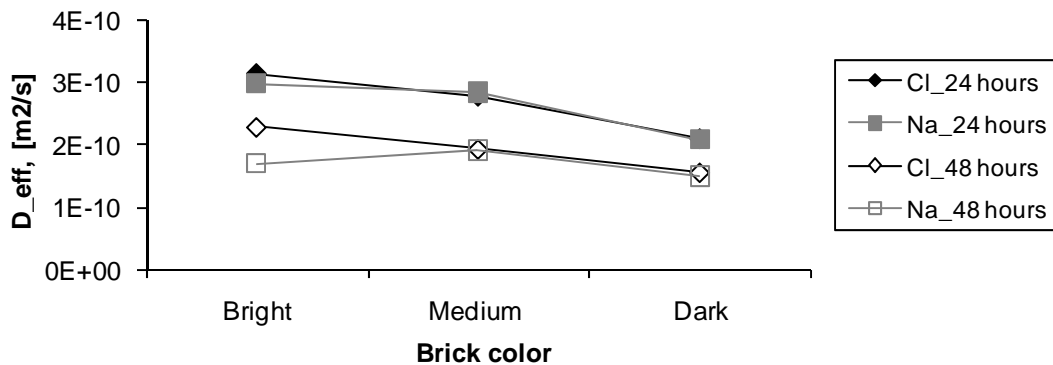


Figure 7. Calculated effective diffusion coefficients according to equation IV for the bright, medium and dark colored bricks after 24 and 48 hours. For the calculation is the resistance across the electrode surfaces and the clay neglected.

The decreasing tendency in the effective diffusion coefficient from bright, to medium to the dark colored brick was the same after both 24, 48 hours and seen for both chloride and sodium. Since the effective diffusion coefficients is calculated in relation to the electrolyte concentration and only the initial concentration is known, the effective diffusion coefficient found after 24 hours must be most representative. After 48 hours desalination, there is a lower electrolyte concentration in the pores of the brick, and this is not taken into account in the calculations. After 24 hours the effective diffusion coefficient for chloride was found to: $3.1 \cdot 10^{-10} \text{ m}^2/\text{s}$, $2.8 \cdot 10^{-10} \text{ m}^2/\text{s}$ and $2.1 \cdot 10^{-10} \text{ m}^2/\text{s}$ for the bright, medium and dark colored bricks respectively. In a free electrolyte the diffusion coefficient for chloride is $2.0 \cdot 10^{-9} \text{ m}^2/\text{s}$. The effective diffusion coefficient after 24 hours for sodium was found to: $3.0 \cdot 10^{-10} \text{ m}^2/\text{s}$, $2.8 \cdot 10^{-10} \text{ m}^2/\text{s}$ and $2.1 \cdot 10^{-10} \text{ m}^2/\text{s}$

m^2/s for the bright, medium and dark colored bricks respectively. As expected is the effective diffusion for both Na and Cl in the same order of magnitude since equal amounts of anions and cations have been discharged at the two electrodes [Laidler, 2003]. In the present experiments with an initial chloride content of 1.0 wt% added as NaCl, the sodium content was 0.65 wt%. At such high sodium content, exchange with sodium from the electric double layer is insignificant and hence not taken into account. In a free electrolyte the diffusion coefficient for chloride is $2.0 \cdot 10^{-9} \text{ m}^2/\text{s}$ and $1.3 \cdot 10^{-9} \text{ m}^2/\text{s}$ for sodium [Atkins, 1994]. Toumi et al. (2007) estimated on basis of [Andrade, 1993] the effective diffusion coefficient in bricks to $8.1 \cdot 10^{-11} \text{ m}^2/\text{s}$ and $16.6 \cdot 10^{-11} \text{ m}^2/\text{s}$ for chloride and sodium respectively. The relative decrease from the highest effective diffusion (bright brick) to the lowest effective diffusion (dark brick) was for both chloride and sodium approximately 30 %.

The difference between the present found effective diffusion coefficients for the different colors can have several reasons. The main reason must be the variation in resistance across the bricks and thereby difference in current strength by constant voltage, since the current determines the number of ions which can be transported. Other reasons could be the material variation for the same brick type as found in the present paper but also between different brick types. Additional could the setup for measuring the effective diffusion affect the result, since e.g. increased total resistance in the setup will decrease the effective diffusion coefficient. During the optimization of the present used setup for electrokinetic desalination, an increased efficiency of a factor 10 was obtained [Rörig-Dalgaard & Ottosen, 2008 C]. Therefore does up to a factor 1.8 and 3.8 higher effective diffusion coefficient for sodium and chloride respectively in the present work for the bright, medium and dark colored bricks compared to the values found by Toumi et al (2007) seems likely.

The measurements of differences between the bright, medium and dark colored brick both regarding resistance and effective diffusion coefficient likely the pore systems influence on the ion transport.

In summary the measurement of the effective diffusion coefficient show significant variations dependent on the pore system and in the pore structures impede on the ion transport. It is shown that the pore structures impede on the ion transport is least in the bright colored, fine porous brick increasing to the coarser medium colored brick and highest for the dark colored coarse brick. These findings are in good consistence with equation II where the pore structures impede on the ion transport is described to be proportional with the porosity and tortuosity and inverse proportional with the constrictivity. In PFM a decreasing numbers of pores were seen in case of increased firing temperatures. This must result in an increased tortuosity (increase in effective diffusion road) and is attributed to be one of the reasons for the lower effective diffusion coefficient at increasing brick firing temperatures. According to equation II a decreasing porosity is described to result in reduced effective diffusion and this was also seen in the present case. The last parameter in equation II, the constrictivity (the effect of resistance from narrow pores) was not examined in the present paper. However, the constrictivitys influence of the effective diffusion may be dependent of the actual ions radii and could therefore be examined by contamination of the bricks with ions of varying ion radii.

The present observations are also in consistency with [Terheiden & Kaps, 2003] which through impedance spectroscopy likely higher diffusion in fine than coarse pores for both bricks and sandstones.

Also Buchwald & Kaps (1999) showed influence from the pore structures on the ion transport of Na_2SO_4 and NaCl in bricks and found a 1.6 times higher ion transport velocity parallel than perpendicular to the extrusion direction in bricks.

5. Conclusion

In the present investigation, bricks fired in a circular kiln (i.e. with uneven temperature distribution) with the colors: bright, medium and dark red were described by macroscopic parameters. The different bricks had significantly differences in open porosity, capillary saturation, dry density and water absorption coefficient. The water absorption coefficient was found both for the entire bricks and for slices of bricks with varying distance to the surface. Major variations in the pore structure from the middle of the brick towards its surfaces were seen. All the measured parameters indicated increasing firing temperatures from the bright to the dark colored brick.

The pore structure of the bricks was examined by PFM with thin sections and showed relative many thin pores for the bright colored brick, fewer and thicker pores for the medium colored brick, and fewer and thicker pores in the dark colored brick.

Measurement of the electrical resistance across bricks at varying firing temperatures indicates increased impede of the ion transport in bricks fired at high temperatures than in bricks fired at lower temperatures. This is related to the pore size and distribution and the electric resistance was smallest in the bright brick with the highest number of thin pores. The effective diffusion coefficient decreased from the bright, to medium to dark colored bricks. The differences in effective diffusion between the bright, medium and dark colored bricks corresponded to the pore structure variation and the differences in the electric resistance measurements.

Related to simulation tools, it is rather problematic to simulate ion transport processes in historic masonry, since significant pore structure variations occur within the construction and variations has to be taken into account. In addition the present investigation only deals with the brick itself and in masonry also the mortar complicates the matter. Also differences in salt concentrations at different heights of the masonry must be taken into account.

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Electromigration versus electroosmosis in a clay brick under non steady laboratory conditions

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Abstract

Deterioration of stones (clay bricks, sandstones ect.) can have several reasons, one being the presence of water and salts.

According to the electrokinetic theory, water and ion transport can be initiated by applying an electric potential gradient across a moist porous material. Both electrokinetic desalination of salt infected stone and electroosmotic drying of stone is possible. The two processes will though not occur simultaneous. Desalination by electromigration should occur first and then subsequently when the ion content in the pore water is low drying by electroosmosis will be initiated.

This paper is focused on documentation of the desalination effect, the drying effect and at which ion concentrations electroosmotic dewatering occurs. The material of the investigation is clay bricks subjected to an applied electric potential. During the investigation non steady ionic contents were present across the setup, similar to the conditions in existing structures.

The effects of an applied potential gradient were investigated in laboratory experiments, with red bricks of the type Falkenløwe, an initial content of 1.0 wt% chloride (added as sodium chloride). Successful desalination was obtained and resulted in very low ion contents below 0.01 wt%. At low ion concentrations the process of electroosmotic dewatering started.

A second experimental row was made with focus on the change between desalination and dewatering with the aim to estimate the electrolyte concentration at which this change occurred. It showed a transition from desalination as the primary phenomena to dewatering as primary phenomena when the average chloride content was reduced to

around 0.01 wt% where the bricks still were capillary saturated and this concentration was termed the “point of starting dewatering”.

The “point of starting dewatering” was on basis of the material property Cation Exchange Capacity, comparison with observations in laboratory scale for another brick type and observations from a pilot plant experiment likely to be general valid.

Keywords

Electroosmosis, electromigration, “Point of starting dewatering”, Cation Exchange Capacity

1. Introduction

By application of an electric DC field across a moist, porous material water and ion transport can be initiated. However, whether a water or ion transport occurs in stones is limited described in the literature.

In a previous work by Friese et al. (1987) the electroosmotic flow was found by measuring the water flow at different electrolyte concentrations in an equilibrium system. The results showed that electroosmotic flow was initiated by electrolyte concentrations below 0.1 mol/L KCl.

However, in praxis most existing structures have varying salt concentrations at different positions and therefore is a system in equilibrium limiting describing for existing structures. The presence of a system in non equilibrium is intensified by application of an electric DC field.

In this paper the laboratory experiments starts with high equilibrium ion contents in whole fired clay bricks and as a function of time and transferred current a system with an uneven ion distribution is developed. The paper aims at clarifying the electrokinetic processes in bricks both theoretically and empirically. It was aimed to clarify the order in which desalination and dewatering occur. Additional was it aimed to likely the general applicability of the results by measuring material properties and by comparison with previously observations in laboratory and pilot plant scale.

2. The electric field

In an applied electric field the current will pass where the lowest resistance is (highest conductivity). The conductivity is mainly dependent on the electrolyte conductivity and the material conductivity (which e.g. is 70-90% dependent of electrochemical properties at the materials surface for the clay types kaolinite and smectite) [Gupta et al., 2007].

The effect of an applied potential can be divided into two groups: ion and water transport and is dependent of the ion concentration in the electrolyte.

In existing structures, there is no clean system and varying ionic contents are present dependent on initial contents and environmental influence. The ionic content can vary significantly from what in electrokinetic connections is inconsiderable, to high and of utmost importance [Rörig-Dalgaard & Ottosen, 2008].

2.1 Electromigration at high ion concentrations

When precipitated salts like sodium chloride (NaCl) is brought in contact with water it dissolves into the ions of sodium (Na^+) and chloride (Cl^-) and increases the electrolyte concentration. By application of an electric DC field to a moist, porous material a positive and a negative electrode is established. Provided that the highest conductivity exists in the electrolyte the ions in the electrolyte will start to migrate as they are attracted to the oppositely charged electrode, see figure 1(a). This phenomenon is termed electromigration [Mitchell & Soga, 1993]. Electromigration proceeds according to the current distribution, meaning transport is ongoing in areas with the lowest resistance. In case of the electrodes are placed at the top the transport of ions will first primarily be from the top area of the brick, since the distance between the electrodes are the shortest. The removal of ions from this area will eventually result in an increased resistance and subsequently the electric field will expand further down, resulting in removal of ions even further from the top (surface). Therefore the electromigration should occur as a function of distance from the electrodes, see figure 1(b).

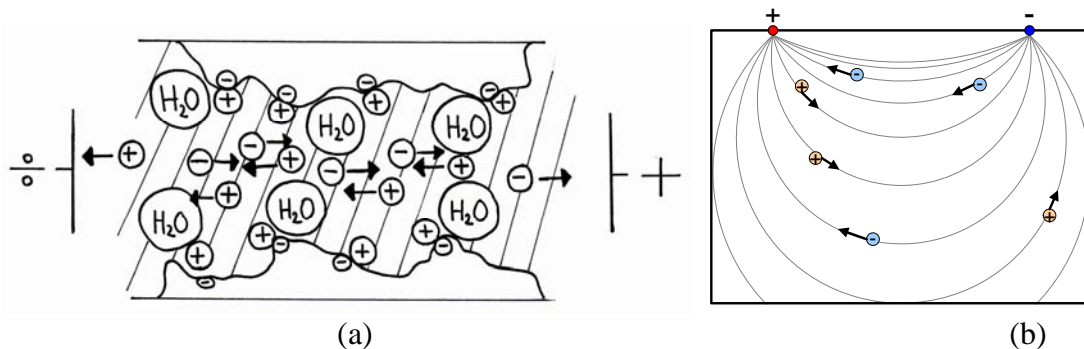


Figure 1. Effects at a high ionic concentration in the electrolyte, by application of an electric DC field. (a) Shown for a single pore (the electrolyte is indicated as the hatched area). The ions are attracted towards the oppositely charged electrodes in the electric DC field (b) Principal sketch of current distribution in a vertical plane along the line of electrodes. Freely after van Nostrand & Cook [1966].

2.2 Electroosmotic water transport at low electrolyte concentrations

2.2.1 The inner surface charge of the material

When a porous material is brought in contact with an electrolyte, chemical reactions occur at the interface between material and electrolyte due to unbalanced force fields. These reactions happen provided: minimum two particles from the material and electrolyte alike are in close vicinity resulting in overlap of force field and provided that the forces are relatively high compared to the particles weight. [Mitchell & Soga, 1993].

The matrix-fluid interface is usually considered to consist of three layers: (i) the material surface which is characterized by the presence of silanol groups (Si-OH) as in case of silica-dominated porous materials filled with a binary symmetric 1:1 electrolyte such as NaCl, (ii) the Stern layer surface which corresponds to the adsorbed cations and

is dependent of bindings between the adsorbed ion and the surface and (iii) the diffuse electrical layer which close to the Stern layer equalize this (meaning surplus of cations) and at the shear between diffuse layer and bulk possess equal quantities of positive and negative ions [Revil & Pezard, 1999], see figure 2 (a). The charge density of the stern layer depends on the surface electrochemical properties of the material and is influenced by: number of sites where the ions can be placed and the equilibrium between adsorption and desorption [Gupta et al., 2007]. The ion adsorption in the Stern layer is dependent on the ionic charge and the hydrated radii: this implies that monovalent cations are generally replaced by divalent or trivalent cation and ions with large hydrated radii are generally replaced by smaller ones [Mitchell & Soga, 1993].

In an electrolyte in the pores of a stone, ions with the same sign as the dominant charge at the material surface (coions) are repelled from the surfaces. Contrary ions with the opposite sign as the surface charge (counterions) are attracted. At equilibrium conditions the net charge density at the mineral surface must be equalized in magnitude and opposite in sign. This equilibrium exists within a small distance from the inner material surface in the so-called electric double layer. The electrical double layer is divided into a fixed (the Stern layer) and non-fixed part (diffuse layer) and the equilibrium is maintained by attraction and repletion in the non-fixed part of the electrical layer [Revil & Pezard.,1999].

Regarding the basis of bricks (silica (SiO_2) from the clay mixture [Brady, 1984]) and pH above 8 negative surface charges are formed (silicic acid (SiO^-)) [Revil & Pezard, 1999].

2.2.2 The electroosmotic phenomena

By application of an electric DC field across a porous material with low electrolyte concentrations, the highest conductivity throughout the system is present in the electric double layer. Since the majority of the co-ions are fixed, a net flow of counter-ions will occur towards the opposite charged electrode, causing turbulence in the surrounding water and resulting in a net water transport towards this electrode, termed electroosmosis [Mitchell & Soga, 1993], see figure 2 (b). Effectively, electroosmotic water transport towards the negative electrode (cathode) has been observed for most porous materials [Ottosen et al., 2008].

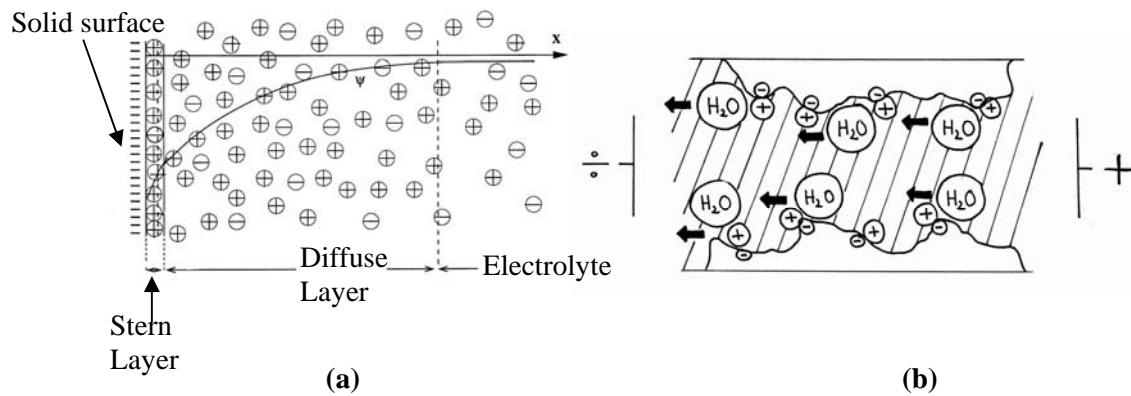


Figure 2. Low electrolyte concentration. (a) Principle illustration of the area close to the matrix-fluid interface adapted from [Gupta et al., 2007] (b) The effect of applying an electric potential across a moist, porous material (the electrolyte is indicated as the hatched area), water transport towards the negative electrode.

The magnitude of the electroosmotic flow is equal in size and opposite to the amount of charge in the pores [O'Brian, 1986]. The water flow can also be characterized through the zeta potential which can be determined through measurement of the streaming potential.

The zeta potential is defined as the potential in the shear plane between the Stern layer and the diffuse layer where liquid motion can occur [Revil & Pezard, 1999]. The zeta potential is macroscopic defined and empirical determined. Contrary the Stern layer is microscopic determined.

High material surface charge results in high Stern layer potentials, resulting in a high possible electroosmotic water transport.

2.2.3 Zeta or Stern layer potential

A link between the zeta potential and electroosmotic flow was aimed in O'Brian (1986); however an unique connection could not be found. The zeta potential was previously thought to describe the electroosmotic transport sufficiently. Meanwhile O'Brian (1986) reported some discrepancies between measured streaming potential and zeta potential when using different measurement methods and suggested that the ions in the Stern Layer should be taken into account.

Results obtained with a model for the average Stern layer potential as a function of ion concentration in the electrolyte by different zeta potentials showed consistence between the zeta potential and the Stern layer potential at low ion concentrations. However, at higher ion concentrations and higher zeta potentials the Stern layer potential was 2-3 times higher than the zeta potential [Gupta et al., 2007].

2.2.4 The influence from pH and salinities on Zeta and Stern layer potential

Both the Stern layer potential and the zeta layer potential are dependent of salinity and pH.

From the point of zero charge (which is pH 3 for silica surfaces) the Stern layer potential is steady increasing [Mitchell & Soga, 1993]. The Stern layer potential decreases by increasing electrolyte concentrations; however the Stern layer potential is not negligible even at high electrolyte concentrations [Revil & Pezard, 1999].

The zeta potential increases by increasing pH [Revil & Pezard, 1999]. The electrolyte concentration is strongly determining for the zeta potential, resulting in high zeta potentials at low electrolyte concentration and no zeta potential at high electrolyte concentrations [Revil & Pezard, 1999]. The zeta potential is also temperature dependent; a 30°C temperature increase can lead to 50% increase in the zeta potential [Revil & Pezard, 1999].

2.3 Electrokinetic across a porous material

The result of an applied electric DC field across a moist, porous material is that in case of high electrolyte concentrations, the highest conductance is in the electrolyte resulting in electromigration induced desalination. Whereas in case of low electrolyte concentrations, the highest conductance is in the electric double layer and results in an electroosmotic water transport.

Additionally to the desired effects described in section 2.1 and 2.2, some undesirable side effects: pH changes [Demberger, 1991], [Auras & Melisa, 2002] and decreasing electrokinetic effects [Castellote et al., 2000], [Ottosen et al., 2006B] occur as a part of the electrical circuit, when electrons in the electrodes are transformed into ions in the liquid by electrode reactions. However, optimization and hindering side effects has been shown possible [Rörig-Dalgaard & Ottosen, 2008B].

3. Experimental

3.1 Bricks for the investigation and their pretreatment

The bricks used in the experiments are made for renovation purpose of older buildings (handcrafted, fired in a circular kiln) by Falkenløwe, Denmark. Comparing investigations have shown similar properties (regarding pore size distribution and porosity) between original Danish medieval bricks and Falkenløwe bricks [Larsen, 1996]. The saturation coefficient of the bricks used in the experimental work was 12.6 +/- 0.4 wt% (found by submerging the bricks into a solution for 3 days). The dimension was approximately 28 cm x 7 cm x 14 cm (Munkesten, the old Danish format). The dry mass of the bricks were 5032 +/- 63 g. The pH was initially 9.2 +/- 0.1 and 8.6 +/- 0.1 after addition of 1.0 wt% chloride.

The present investigation was carried out with a high, although frequently measured ionic content of 1.0 wt% chloride to illustrate the methods usefulness in a typical situation. To obtain a 1.0 wt% chloride, the bricks were submerged in a sodium chloride solution for 3 days. The solution was made by introducing 79.61 gram sodium chloride into a 1 +/- 0.0004 L measuring flask. Subsequently the bricks were carefully wrapped in plastic film to minimize evaporation.

3.2 Sampling Description

Presence of damaging salts in masonry is mainly a problem that appears during the lifetime of the building. To make a diagnosis of existing buildings in Denmark, 10 mm drilling samples are made. As this method is used on existing buildings it is also used in the laboratory experiments to make comparison possible with real conditions. The size of 10 mm is a compromise to obtain representative results on both water and ions contents and still minimize the size of the drilling holes.

To map the chloride movements within the electric field (taking the field lines (figure 1b) into account), 9 drilling samples were made from each brick, by dividing the brick into 3 equal pieces both vertically and horizontally. The drillings were made in the middle of each of these 9 pieces, figure 3.

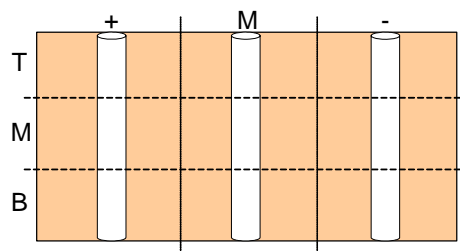


Figure 3. Principle drawing of the sampling. Each brick is divided into 3 pieces both horizontally and vertically. The upper third closest to the electrodes is called top piece and the brick pieces just below the positive electrode is called + e.g. upper left piece is called +T.

3.3 Analytical

Simple extractions in distilled water were made to evaluate concentrations of Cl^- and Na^+ . The drilling samples were dried by 105°C until equilibrium (one day) and the water content was calculated as weight loss. The extractions were made with the drilling powder from each position (around 5 g) and 12.5 mL distilled water. The suspensions were agitated for 24 hours without air supply since this gave the most reproducible values [Rörig-Dalgaard 2008]. The pH was measured with electrode MeterLab® CDM220 after settling of the agitated samples for 5 minutes.

The chloride content was measured by a titrator (Metrohm 716 DMS Titrino). The Cation Exchange Capacity (CEC) was measured with a method corresponding to EPA standard method 9080 at pH 7 on brick powder dried at 105°C until equilibrium [EPA, 1986].

3.4 Setup

The two electrode units were both placed on the bricks long, narrow side. Two holes were cut in the plastic, in each end of the brick in which the electrode units were placed. The holes each had an area of $5.5 \text{ cm} \times 7.0 \text{ cm}$. A flexible plastic form was used to ensure the right amount of poultice throughout all the experiments. These plastic forms covered the area between brick and electrodes. The plastic forms had a height of 3.5 cm. To obtain an efficient desalination, a special developed buffer poultice was used consisting of kaolin clay, buffer component and distilled water. This poultice is described in details in Rörig-Dalgaard & Ottosen (2008B). The applied current was 80 mA in all the experiments corresponding to 2.1 mA/cm^2 electrode. See figure 4.

The electrodes were stainless steel mesh electrodes.



Figure 4. Laboratory setup where the electrodes (and poultices) both are placed on the bricks long, narrow side.

3.5 Experimental overview

Experiments with an applied current of 80 mA (2.1 mA/cm^2 electrode) and 1.0 wt% chloride ($\sim 1.36 \text{ mol/L}$ electrolyte concentration) were carried out. The only varied parameter was the duration time (table 1).

Table 1. Experimental overview.

| Experiment | Duration [Weeks/days] | I [mA] | U [V] |
|------------|--------------------------|-----------|----------|
| W 1 | 1 Week | 80 | 8-12 |
| W 2 | 2 Weeks | 80 | 10-36 |
| W 3 | 3 Weeks | 80 | 9-138 |
| W 2.6 | 2 Weeks, 4 days | 80 | 10-105 |
| W 2.7 | 2 Weeks, 5 days | 80 | 10-39 |
| W 2.9 | 2 Weeks, 6 days | 80 | 9-39 |
| W 3b | 3 Weeks | 80 | 9-90 |
| W 3.1 | 3 Weeks, 1 day | 80 | 9-88 |
| W 3.7 | 3 Weeks, 5 days | 80 | 8-104 |

The voltage was lowest in the beginning of the experiments and increased during the treatment.

4. Results and discussion

The following results clarifies whether the electroosmotic water transport is (a) ongoing simultaneously with desalination, (b) whether it will start after almost complete desalination of some parts or if (c) low ion concentrations must be achieved in the whole brick before the electroosmotic drying is initiated (section 4.1).

The accurate transition between ion and water transport was found by additional experiments (section 4.2). Finally the general validity of the transition between desalination and electroosmotic water transport is discussed based on measured material properties and observations by previous work (section 4.3).

4.1 Desalination versus electroosmotic water transport

An experimental series (W1, W2 and W3) was initiated with the aim of obtaining the lowest possible ionic content and to follow the desalination and water transport. The final chloride and water contents after the experiments are shown in figure 5.

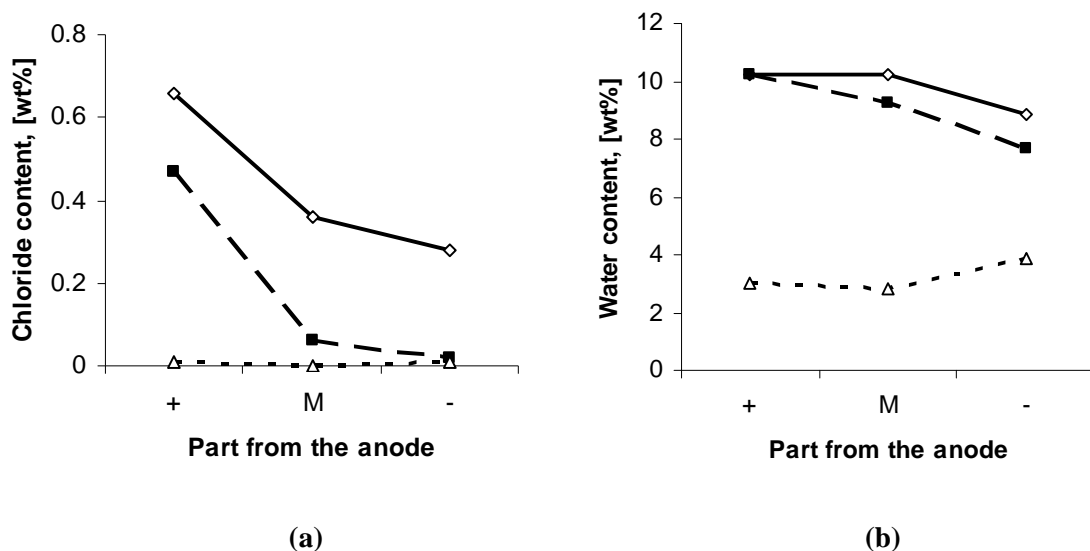


Figure 5. (a) Remaining chloride content (b) Water content after \diamond 1 week (W1) \blacksquare 2 weeks (W2) \triangle 3 weeks (W3). Each point is an average of three vertical taken samples either: below the anode (+), the middle (M) or below the cathode (-).

The average chloride content decreased from initially 1.0 wt%, to 0.005 wt% after three weeks. Regarding the water content there were no significant changes in the first two weeks (figure 5(b)) were there still were high ion contents in some parts of the brick. A minor decrease in water content was measurable within these first two weeks and was ascribed to evaporation. Contrary, after three weeks (W3), significantly lower water content was measured after ended experiment in all the 9 drilling samples. Comparison of the remaining chloride content with the suddenly decrease in water content between second and third week indicates that after almost complete desalination of the brick, drying by electroosmosis occurred and resulted in the low water content. This is supported by the change in slope coefficient which is negative seen from the anode towards the cathode after the first 2 weeks, whereas a positive slope coefficient was

seen after 3 weeks (figure 5 (b)). In case of electroosmotic flow in bricks a transport of water towards the cathode is expected, meaning a positive slope coefficient from the anode towards the cathode as seen after three weeks (W3) in figure 5(b).

4.2 The transition between ion and water transport

Experiments W1-W3 indicate that the electroosmotic water transport was initiated after complete or almost complete desalination was obtained and that very low chloride contents in one area is not sufficient to generate a measurable electroosmotic flow through the whole bricks.

Experiments W 2.6, W2.7 and W2.9 were initiated, with focus on the transport processes by average chloride contents between 0.18 wt% and 0.005 wt% (meaning the interval between the final levels of experiment W2 and W3), see figure 6.

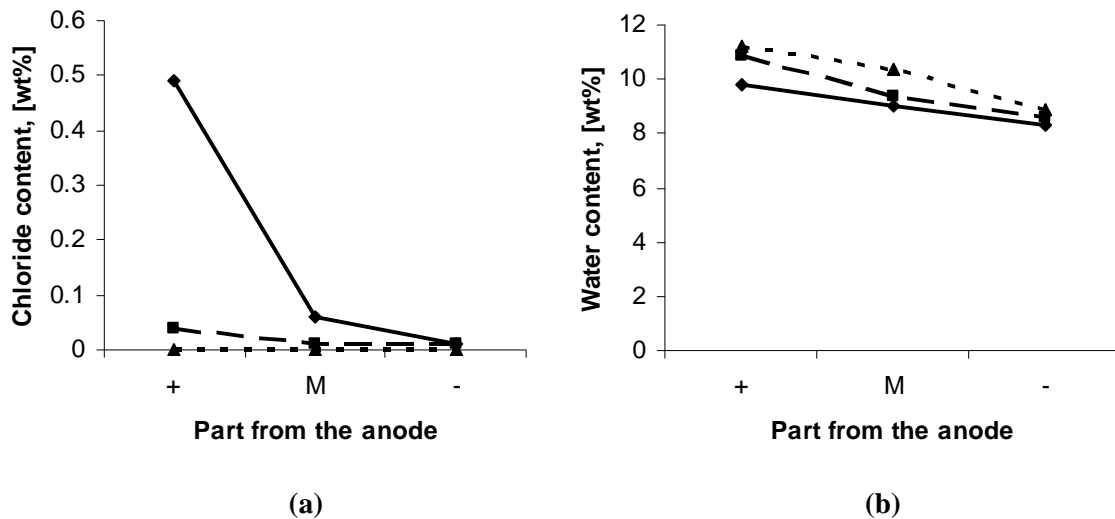


Figure 6. (a) Chloride content. (b) The corresponding water content after ♦ 2 weeks + 4 days (W2.6) ■ 2 weeks + 5 days (W2.7) ▲ 2 weeks + 6 days (W2.9). Each point is an average of three vertical taken samples either: below the anode (+), the middle (M) or below the cathode (-).

The chloride content after 2 weeks + 4 days, 2 weeks + 5 days, 2 weeks + 6 days was 0.18 wt%, 0.02 wt%, and 0.009 wt% respectively without any measurable dewatering effect. However, the dewatering process might have started to a minor insignificant content at a chloride content of 0.009 wt%.

Additional experiments W3b, W3.1 and W3.7 were initiated. These experiments were carried out until electroosmotic water transport was observed (in shape of water drops underneath the wrapping of the plastic film). The average measured chloride and water content after ended experiment W3b, W3.1 and W3.7 are plotted together with all the other results on chloride and water contents in figure 7.

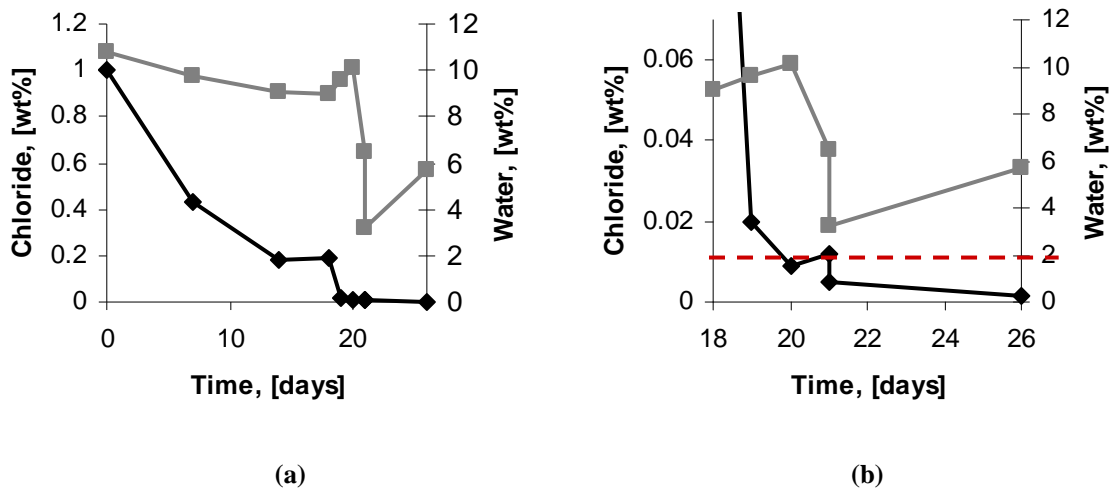


Figure 7. Average chloride and water content in the bricks as a function of time. (a) For the whole period. (b) A close-up for the period where the dewatering starts. Black points are measured chloride contents and gray points are measured water contents. Each dot is an average of all the nine measurements from each experiment. The red dotted line indicated the “point of starting dewatering”.

The average chloride content is reduced continuously (black line) as a function of time. Contrary the average water content was steady the first 20 days and then suddenly decreases.

On basis of the results shown in figure 7, reduction in the water content seems to be initiated at an average chloride content of 0.012 wt% (W3.b) and continues below this ion content. However, even though a reduction of the average chloride content to 0.009 wt% in W2.9 was obtained no dewatering effect was observed. This suggests that the shift between electromigration as the primary process to electroosmotic water transport is around 0.01 wt% anions (dotted line) but with some variation dependent of the specific brick. Since the water reduction starts at chloride contents below approximately 0.01 wt% it seems reasonable to define this limit as the “point of starting dewatering”. There seems to be some variations in the “point of starting dewatering” which is attributed to material variations even for the same brick type. This is e.g. seen for the measurements after 26 days which slightly differs from the tendencies. The result must be a specific material dependent “point of starting dewatering”. Though, it can also be argued that determination of a precise limit is of minor relevance when working with a natural product as clay bricks and bricks in constructions exposed to varying environmental exposure as found by Rørig-Dalgaard & Ottosen (2008).

After reaching the “point of starting dewatering” chloride was still transported to a minor extent. Simultaneous marginal desalination and water reduction will therefore occur below the ion concentration corresponding to the “point of starting dewatering”. These results indicates that desalination and water transport are non parallel processes at high electrolyte concentrations, and that desalination to a low electrolyte concentration must occur, before the electroosmotic water transport starts. For this reason it seem reasonable to term the shift between ion and water transport “point of starting dewatering”.

4.3 The material properties influence on the “point of starting dewatering”

To assess the general applicability of the “point of starting dewatering” in relation to different brick types, different bricks inner surface properties were examined and compared with previous observations during electrokinetic treatment in laboratory and pilot scale.

In the present investigation the surface properties were investigated at low ion contents (mainly new, non salt contaminated bricks) and measurement of the Stern layer potential for determination of the electroosmotic effects does therefore seem reasonable according to O’Brian (1986).

The Stern layer capacity (surface charge density per unit pore volume) corresponds to the adsorbed cations to the material and can according to Mitchell & Soga (1993) be measured as cation exchange capacity (CEC) when water density and water content is taken into account. CEC is according to the used standard determined at pH 7 and the found values are therefore solely a function of the material, whereas the Stern layer capacity also can be a function of pH and salinity (section 2.2). CEC was determined in doublets for different brick types: yellow, red, new and old (table 2).

Table 2. Cation Exchange Capacity (CEC) for different brick types.

| Brick name | Color | Age | CEC [meq/100 g dry brick] | Average CEC [meq/100 g dry brick] |
|-----------------|--------|-----------|------------------------------|--------------------------------------|
| Wewers gul | Yellow | New | 2.2-4.1 | 3.1 +/-1.3 |
| Optiroc gul | Yellow | New | 1.4-2.6 | 2.0 +/- 0.8 |
| Antik gul | Yellow | 110 years | 1.6-2.4 | 2.0 +/- 0.6 |
| Wewers rød | Red | New | 1.3-1.6 | 1.5 +/- 0.2 |
| Lundegården rød | Red | New | 0.8-0.9 | 0.9 +/- 0.1 |

The measured CEC values are all within the same order of magnitude and shows repeatability of the results. A variation of a factor 3 was measured between the highest and the lowest CEC values.

Based on the measured values in table 2, there seems to be a tendency for higher CEC values for yellow bricks than for red bricks in the order of a factor 2. Since the CEC values represent the Stern layer capacity which again initiates the electroosmotic flow, a two times higher electroosmotic water flow should be expected in yellow bricks than in red bricks at the same ion concentrations (related to the weight of the brick). Likewise, the electrolyte concentration steady decreases the Stern layer potential (section 2.2.3) and affects the actual Stern layer potential. On basis of the measured CEC values shown in table 2 a two times higher electrolyte concentration should be expected at the “point of starting dewatering” in case of yellow bricks than for red bricks.

The measured differences in CEC between the different brick types are ascribed to differences in the raw materials. However, such small differences as measured between red and yellow bricks is expected in existing structures, related to the actual location and the result will therefore most probably be similar “point of starting dewatering” for different brick types. Therefore it is assumed that the “point of starting dewatering” is within the same narrow level and therefore rather material independent. It must be noticed that the used CEC measurement method is developed for soil which have significantly higher values (e.g. is CEC in a typical Danish soil 4-26 meq/100g [Jensen et al., 2006]). During some of the measurements the found CEC values were within the

range of deviation and due to these high uncertainties not included in table 2. The deviations could be caused by inhomogeneous bricks and it could indicate that a more precise measurement method would be appropriate for bricks.

A pilot experiment was conducted on a wall with high water contents (7-15 wt%) [Ottosen & Rörig-Dalgaard, 2006]. Concentrations of 0.1-0.4 wt% nitrate and 0.15 wt% chloride content were measured in some single points. These ion contents exceed the threshold values from the ÖNORM B 3355-1 to a minor extend and desalination was therefore desirable. After ended treatment accumulation of structure damaging ions was measured in the electrode units (0.04-0.09 wt%) [Ottosen & Rörig-Dalgaard, 2006] indicating that even at low to moderate ion contents the transport process results in desalination. Whether electroosmotic water transport also occurred to a minor content is uncertain. However it must be noticed that these results were obtained in an inhomogeneous system with both clay bricks and mortar which might influence the “point of starting dewatering”.

During electrokinetic desalination of the brick type “Wewers yellow” in laboratory scale decreased water content was measured in experiments with a final average anion content of 0.006 and 0.0009 wt% chloride, contrary to experiments with a final average anion content of 0.03 and 0.009 wt% chloride where no dewatering effect was measured [Ottosen & Rörig-Dalgaard, 2007]. This indicates a “point of starting dewatering” between 0.006 and 0.009 wt% anions in agreement with the present found “point of starting dewatering” on 0.01 wt% anions in section 4.2 showing no significant difference between the red brick produced by Falkenløwe and the yellow brick produced by Wewers.

Friese (1984) measured the streaming potential (zeta potential) in a 1:1 electrolyte (e.g. NaCl) with different concentrations and found the streaming potential to be neglectable when the concentrations reached 0.1 mol/L whereas in 1:2 electrolytes (e.g. CaCl₂) the streaming potential already was neglectable at electrolyte concentrations between 0.01 and 0.005 mol/L. Taking the porosity in the Falkenløwe bricks into account, an electrolyte concentration of 0.1 mol/L corresponds to an ion content of 0.0007 wt% chloride. This value is approximately 14 times lower than the suggested limit in the present investigation and could be an indication on the difference between theoretical obtainable values under steady conditions and values obtained in more applied non steady conditions.

Threshold values for salt concentrations are related to the dry mass of the material (Önorm B 3355-1), and are therefore only influenced by the measured salt concentration. Friese (1984) suggests a limiting electrolyte concentration which must be related to both water and ion concentration measurements. Additionally, existing structures most probably consists of both 1:1 and 1:2 electrolytes it seems circumstantial to measure: ion type, ion content and water content in order to find the “point of starting dewatering” since the ion concentrations will vary throughout the structure. For practical investigations it seems more appropriate to relate the “point of starting dewatering” to the ion content per dry mass and recognize that this point is within a minor interval dependent on the actual structure and ion type.

The above results and observations are mainly obtained with Falkenløwe bricks. An extension of the investigation, to a setup with both brick and mortar could lead to a higher variation in the value for the “point of starting dewatering”. However, by applying the anode and cathode electrode unit at the same side of the brick masonry

structure there will always be a possibility for transport solely inside a brick if the electrodes are placed with a distance shorter than the length of the brick.

5. Conclusion

The present laboratory experiments document the electrokinetic processes in laboratory scale under non steady laboratory conditions. It was shown that the desalination process is dominating at high electrolyte concentrations followed by dewatering at low electrolyte concentrations. The desalination and dewatering processes proceed mainly one at a time and not parallel. The concentration at which the shift between desalination by electromigration and electroosmotic dewatering occurred was termed the “point of starting dewatering” and found to be 0.01 wt% chloride for the brick type Falkenløwe. Comparison with previous results and measurements of different types of bricks surface properties (Stern layer potential found by CEC measurements) suggested that the found “point of starting dewatering” seems to be general representative.

Since ion reduction from a high problematic content (1.0 wt%) to a content well below the threshold value (0.005 wt%) for chloride and a water reduction from 9 wt% to 3 wt% was achieved just within 3 weeks it is shown that the electrokinetic processes are effective in fired clay bricks.

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Development of a poultice for electrochemical removal from bricks – Effects and side effects

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Abstract

Salt induced deterioration of murals in churches has increased within the last decades in Denmark. At present two different techniques are applied: poultices or establishment of climate chambers. Both techniques can result in ion transport away from the valuable surfaces with murals, but satisfying desalination cannot be obtained according to conservators from the Danish National Museums mural preservation section. The treatment is therefore only temporary and not a lasting solution.

In the present paper the possibility for salt removal by utilizing a well known and accepted transport process, electromigration, is investigated, i.e. movement of ions in a solution in an applied electric DC field. Most Danish church vaults are made from porous clay bricks. The salt infected vaults are moist and the electric field can therefore pass in the pore solution. Electromigration is expected to be an efficient transport mechanism for desalination of the church vaults. The advantage of using an applied electric DC field is that the ions are affected directly and they are therefore less poultice and substrate dependent compared to other desalination methods.

An experimental laboratory setup was designed to approximate real conditions and with ion contents corresponding to normal heavily polluted church vaults (1.0 wt% Chloride, added as NaCl). A constant current of 40 mA was applied to the brick until the resistivity increased significantly or until satisfying desalination was obtained.

During the electromigration process acid and base is produced at the electrodes due to electrode reactions. Acid (H^+) and base (OH^-) production can change the pH in the brick resulting in increased ion dissolution (weathering) and decreased electromigration efficiency of the damaging ions out of the brick. In experiments where no precautions were taken, the extent of pH changes was significant and the electrode reactions did hinder a satisfyingly high desalination effect. New electrode units were developed to hinder pH changes in the brick during the treatment. They consisted of metal net, kaolin clay and buffer components which were able to neutralize the produced acid and base.

The results showed good ability to retain neutral pH values in the substrate. Also the desalination process continued until a low and harmless salt content was reached with the new electrode units.

Keywords

Brick, electromigration, desalination, pH stability, sodium, chloride

1. Present methods for desalination of murals and previous investigations on the use of electromigration

Within the last decades increased and fast deterioration of murals in some churches has been seen. The problem is changed user conditions as e.g. heating for services resulting in varying relative humidity's and presence of salts, especially sodium chloride in the vaults [Larsen, 1999]. According to conservators from the Danish National Museums mural section two techniques are presently applied in Denmark to decrease deterioration of salt infected church vaults: wet or dry poultices or establishment of climate chambers. This paper is focused on the development of a method based on electromigration, which on the contrary to the other methods acts directly on the ions. As the ions are directly affected by the electric field the method is thought to be more independent of substrate material characteristics and ion content than the poultice methods compared to the two present used methods.

Only few investigations have previously been made on desalination with electromigration. Friese & Birkenhofer (1985), Friese & Protz (2005) reports a desalination effect by use of such method, but the adverse effects from the electrode processes are not mentioned. Demberger (1991) points out that the adverse effects are not controlled as discoloration close to the anode occur and pH values of 1 near the anode and pH values of 12 near the cathode. An investigation made by Auras & Melisa (2002) measured similar pH changes in pilot: pH 3 close to the anode and pH 10 close to the cathode and a chloride reduction of 1.5 wt% until a depth of 7 cm in brick masonry.

Such significant pH changes alter the original material significantly [Krenkler, 1980], [Schumann, 1997] and cannot be accepted especially not in connection with cultural heritage.

In the field of electrochemistry, adverse effects due to electrode reactions are well known and it is also known that they hinder optimal ion transport within the electric field. In connection to remediation of soil, fly ash and wood, anion and cation exchange membranes have been used to separate the substrate and the electrodes to avoid the pH changes of the material and thereby also to optimize the remediation process. The electrodes are placed in an adjustable liquid, which is neutralized by addition of different components [Ottosen et al., 1997]. During chloride removal from concrete the developed base front is advantageous for protection of the concrete reinforcement and is therefore allowed to spread freely [Banfill, 1997].

Preliminary experiments with a chloride content of 1.5 wt % showed significant chloride reductions to a mean concentration of 0.44 wt% chloride in 4 weeks [Rörig-Dalgaard & Ottosen, 2007] and clarified that also in the case of heavily contaminated bricks the electromigration method is an efficient method.

For assessment of damaging salt concentrations only one set of threshold value is available at present, ÖNORM B 3355-1 [Österreichisches Normungsinstitut], and this norm describes chloride contents above 0.1 wt% to be damaging and subject to a desalination action. This norm is by some considered to advice very low and maybe to low ion concentrations, but it is evident that the lowest possible salt content is desirable. The aim of this work was to document the desalination effect of electromigration, clarify the adverse effects and to make new developments to hinder these adverse effects.

2. Electromigration and electrode reactions

2.1 Electromigration

When salts is brought into contact with water they dissolves and in the case of NaCl into the ions sodium (Na^+) and chloride (Cl^-). When a current is applied a positive and a negative electrode is established and the ions in solution will be attracted to the electrode of opposite sign and move according to their charge, see figure 1.

This phenomenon is termed electromigration. By use of electromigration a controlled ion transport is possible in porous wet materials like bricks. The idea is to transport the damaging ions out of the church vaults bricks and mortar into an accumulating layer which can be removed after ended treatment.

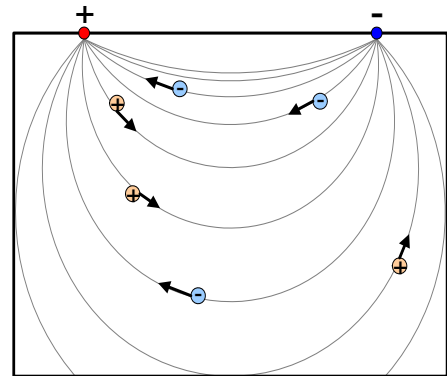
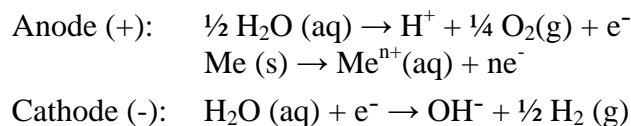


Figure 1. Principal sketch of potential and current distribution in a vertical plane along the line of electrodes with ion migration. Freely after [van Nostrand 1966]

2.2 Electrode reactions

An electric circuit in a wet brick is maintained by electrons in the electrodes which though electrode reactions are transformed to ions in the pore solution and visa versa. Among others the electrode reactions will result in varying extends of acid (H^+) formation and metal decomposition at the anode and base (OH^-) formation at the cathode [Acar, 1993]:



If no precautions are taken against the acid and base production at the electrodes, pH of the brick will change. Exposure of acid to ceramic material (roofing tiles) resulted in increased porosity [Radeka, 2007] and thus acid is known to damage the ceramic material. The mortar is supposed to be even more vulnerable against acid influence. In addition, the desalination effect of the method will most properly decrease as the current will transport H^+ and OH^- instead of the contaminating ions (Na^+ and Cl^-), since H^+ and OH^- possess exceptionally high ionic mobility [Laidler et al., 2003], [Ottosen et al., 2008]. Reduced transport number and thereby also chloride transport has been measured during desalination of concrete with electromigration mainly attributed to the OH^- generation and its higher mobility. This implies a limit in the amount of extraction and

complete electromigration desalination is impossible if no action is taken against this OH^- generation when dealing with concrete [Castellote et al., 2000].

As murals are an important part of the Danish cultural heritage, special precautions has to be taken when introducing electromigration as a renovation technique as actions impossibly can be redone. Adverse effects are even more important to control than effects (according to the Danish cultural heritage authority). Therefore the crucial point of this investigation was whether pH changes can be satisfying minimized.

Previously pilot plant experiments with desalination of masonry (7 days, 1.14 mA/cm electrode) showed no pH change close to the anode where a brickwork clay with high buffering capacity was used to neutralize the acid, though at the same time pH increased from 8.4 to 9.1 close to the cathode [Ottosen et al., 2007 A]. The extend of pH changes and the importance of taking the pH changes into account will be clarified in the following experiments.

3. The poultice

3.1 The basic poultice

For the extraction of the damaging ions during the desalination with electromigration an accumulating material for the ions (poultice) is needed between the metallic electrodes and masonry. A traditional poultice can consist of one or more of the following components: cellulose, clay (bentonit, kaolin), newspaper, sand, filler etc. [WTA]. The idea of the present work is to combine use of the poultice and electromigration methods, and improve the poultice to optimize the conditions during electromigration.

Following demands were made to the electromigration poultice:

- Clean poultice with low initial ion content: to isolation of the electromigration effects, make them more clear during the documentation phase and hinder transport of new ion into the brick.
- Good electrical conductivity to maintain the electric circuit.
- Good workability and thereby contact to the brick.
- Limited shrinkage to maintain the god contact to the brick during treatment.

Contrary to traditional desalination with poultices, the material characteristics (e.g. capillarity) for both poultice and brick and their differences is not essential when utilizing electromigration for ion transport, since the driving force is the current and not diffusion or convection. This fact makes the method more robust compared to other desalination methods.

Traditional kaolin clay was chosen as basis material for the investigations due to its purity, low shrinkage, good workability and conductivity when distilled water is added. The liquid to solid ratio between kaolin clay and distilled water was decided experimentally through series with varying ratios made in order to obtain the right consistency of the mixture.

3.2 Limitation of the acid effect by the anode - neutralization

During the application of current acid is produced at the anode as described in section 2.2. The H^+ is inevitable produced as a part of the electric circuit at the anode; however, hindering the produced H^+ in entering the brick is possible. Deduced from soil

remediation experiments, presence of carbonate is known to limit the acidification produced by the electrodes by neutralization [Ottosen et al., 2005]. Previously experiments have been carried out with electrode units consisting of clay from the local brickwork rich in carbonate (17-18 wt%) working as a combined accumulation layer and neutralization material and showed good neutralizing effects during a pilot plant experiment, 9 days at 0.16- 0.47 mA/cm electrode [Ottosen & Rørig-Dalgaard, 2006]. The carbonate in clay used for brick production exists as CaCO₃. During reaction between CaCO₃ and acid (H⁺), CaCO₃ decomposes (CO₂(g) + H₂O + CaCO₃ ↔ Ca²⁺ + 2HCO₃⁻) [Appelo & Postma, 1993]. The reactions during the dissolution process causes the ability to oppose changes in pH by addition of acid, a so-called buffer action [Atkins, 1990]. The previous pilot plant experiment was carried out with a fixed carbonate content in the clay independent of the applied current, duration and thereby the actual produced H⁺ concentration. In the present paper the idea was to calculate the produced acid and neutralize it by addition of the actual needed neutralizing component. The total capacity of the buffer component and thereby neutralization time is dependent of the buffer components capacity. One mole H⁺ is produced by use of one mole e⁻ which means that the H⁺ production is dependent of the applied current. By calculation of the consumed coulomb amount (Q) by a specific current strength (I) and duration time (t):

$$Q = I \cdot t$$

Conversion of coulomb amount to mole H⁺

$$n_{H^+} = \frac{Q \cdot n_{H^+}}{F \cdot n_{e^-} \cdot n_{H^+}}$$

The H⁺ concentration to be neutralized was calculated. Contrary to the previous work, neutralization need was calculated before the experiment was carried out (dependent of current strength and duration time) and *added* as buffer material to the basis material (kaolin clay) in the calculated amount to ensure the needed neutralization effect. Carbonate is present in several compounds. Calcium carbonate was chosen as it is a harmless component and has a very low solubility. Calcium carbonate is also present in the original clay mixture for brick production. The poultice which solely consists of kaolin clay and calcium carbonate is a clean system. It makes it easier to control the processes in comparison to the brickwork clay, which do not have a well described chemical composition. Taking the carbonate percentage in calcium carbonate into account:

$$\% \text{ CO}_3 \text{ in CaCO}_3: \frac{m_{\text{CO}_3^{2-}}}{m_{\text{CaCO}_3}} = \frac{60,01g}{100,09g} \sim 60 \%$$

the exact mol carbonate could then be added to the clay mixture taking into account:

$$m_{\text{CO}_3^{2-}} = n_{\text{CO}_3^{2-}} \times M_{\text{CO}_3^{2-}} \times \% \text{CO}_3$$

Where $n_{\text{CO}_3^{2-}} = n_{\text{H}^+}$ to be neutralized.

Since both the anode and cathode are placed at the same side of the brick, the current distribution is non-uniform, resulting in a non-uniform consumption of buffer component and undesired pH changes. Therefore a factor of 1.3 was multiplied to the needed calculated carbonate amount to be on the safe side.

3.3 Limitation of the base effect by the cathode - neutralization

To maintain the electric circuit OH⁻ is produced as a part of the reactions at the cathode, as described in section 2.2. The extent of these changes was investigated in a clarifying experiment (section 4.1) which showed that precautions must be taken to avoid OH⁻ in entering the brick.

Again the demand was to neutralize the produced OH⁻ by the electrode (cathode). Use of buffer solutions was again considered to maintain a stable pH. For neutralization of the base an acid was searched and in addition a weak acid. Contrary by contact between a strong acid and a building material pH changes will occur at least at the interface between the building material and the strong acid. In buffer solutions were the molar concentration of the acid and its conjugated base are approximately equal pH is close to the pK_a value (pK_a = -log₁₀(acidity constant)) for the acid [Chang, 2005]. Therefore a weak acid with a pK_a around 5-7 was searched. Two possibilities are:

- Carbonic acid (H₂CO₃) with a **pK_a of 6.4** [Chang, 2005]
- Acetic acid (CH₃COOH) which has a **pK_a of 4.7** and a buffer capacity between pH 3.8 and 5.8. [Chang, 2005], [Helt & Rancke-Madsen, 1991]

Buffer solutions have normally buffer capacity within a range of 2 pH-units, which means pK_s +/- 1 pH [Helt & Rancke-Madsen, 1991]. Both of these weak acids seem therefore useful to maintain pH around 5-7.

Another essential issue which has to be taken into account is the request for a limited amount of new ions being allowed to enter the brick during the electromigration process. As carbonic acid (H₂CO₃) is forming H⁺ and CO₃²⁻ when dissolved and carbonate is one of the common components in harmful building salts it is a problematic choice to use this acid even though its pK_a value is closer to neutral than acetic acid. Acetic acid (CH₃COOH) is dissolved into H⁺ and CH₃COO⁻. CH₃COO⁻ is not known to be a harmful ion in brick masonry and was for this reason interesting a possible choice. Entering of the buffering component (e.g. CH₃COO⁻) into the brick can occur by diffusion due to concentration gradients and for this reason the lowest possible diffusion coefficient is favourable.

In table 1 the molar ionic conductivities from [Laidler et al., 2003], [Zimmerman & Wood, 2002] are converted to diffusion coefficient for the dominating ions in the system by [Laidler et al., 2003] by:

$$D = \frac{R \cdot T}{F^2 \cdot |z_i|} \cdot \lambda^\circ$$

Where R is the molar gas constant (8.3143 J · mol⁻¹ · K⁻¹), T the temperature in Kelvin (K), F is Faradays constant (96485 C · mol⁻¹), z_i the charge number and λ[°] the molar ionic conductivity (S·cm²·mol⁻¹).

Table 1. Molar ionic conductivities and diffusions coefficients for relevant ions.

| | H ⁺ | OH ⁻ | Cl ⁻ | ½ CO ₃ ²⁻ | ½ Ca ²⁺ | Na ⁺ | CH ₃ COO ⁻ |
|---|----------------|-----------------|-----------------|---------------------------------|--------------------|-----------------|----------------------------------|
| λ [S·cm ² /mol] | 349.65 | 198 | 76.31 | 69.3 | 59.47 | 50.08 | 40.91 |
| D [10 ⁻⁵ cm ² /s] | 9.30 | 5.27 | 2.03 | 1.84 | 1.58 | 1.33 | 1.09 |

CH₃COO⁻ has compared to the other ions in table 1 the lowest diffusion coefficient and thereby reduced access to the brick. The relative low diffusion coefficient for CH₃COO⁻ is most probably caused by the ions larger size.

Ion exchange occurs between equivalent amounts of ions to preserve electro neutrality at all times in both the exchanger and solution phases [Grimshaw & Harland, 1975].

This means that by production of 1 mole OH⁻ 1 mole of acetic acid is needed for neutralisation (OH⁻ + CH₃COOH → CH₃COO⁻ + H₂O). Corresponding to the H⁺ production the OH⁻ production also dependent of current strength and duration.

To calculate the needed acetic acid addition to the kaolin clay, the consumed coulomb amount was calculated and converted to mole hydroxide.

4. Experimental

4.1 Bricks for the investigation and their pretreatment

The bricks used in the experiments are made for renovation purpose of older buildings (handcrafted, burned in a circular kiln) by Falkenløwe, Denmark. Previous comparing investigations have shown similar properties (regarding pore size distribution and porosity) between original Danish medieval bricks and the Falkenløwe bricks [Larsen, 1996].

The dimensions of the bricks for the present investigation were approximately 28 cm × 7 cm × 14 cm (named Munkesten), where the 14 cm thickness corresponds to the thickness of an average church vault in Denmark. The dry mass of the bricks are 5032 +/- 63 g. The saturation coefficient was 12.6 +/- 0.4 wt% (found by submerging the bricks into a solution for 3 days). The pH was initially 9.2 +/- 0.1 and 8.6 +/- 0.1 after addition of 1.0 wt% chloride. To obtain a 1.0 wt% chloride the bricks were submerged in a sodium chloride solution for 3 days. The solution was made by introducing 79.61 gram sodium chloride into a 1 +/- 0.0004 L measuring flask. After obtaining the right ion and water content in the bricks, they were carefully wrapped in plastic film to minimize evaporation.

4.2 Setup

The present investigation was carried out with a typical (in relation to salt infected Danish church vaults) ion content of 1.0 wt% chloride to illustrate the methods usefulness in the typical situation. The accumulating layer of the electrodes was placed in a hole cut in the plastic and renewed each 7.th. day. The hole had an area of 5.5 cm × 7.0 cm and to ensure the right amount of buffer clay by all the experiments, a flexible plastic form covering the area between brick and electrodes, in the height of 3.5 cm was applied. The applied current was 40 mA in all experiments corresponding to 1.0 mA/cm² electrode surface. The anode and cathode were both stainless steel meshes. The electrode design was made with focus on protection of the murals in a church vault and as the surface of the murals can be very fragile, electrodes were solely placed on the

upper side of the brick corresponding to placement of the electrodes solely on the upper side of the vault as seen in figure 2.

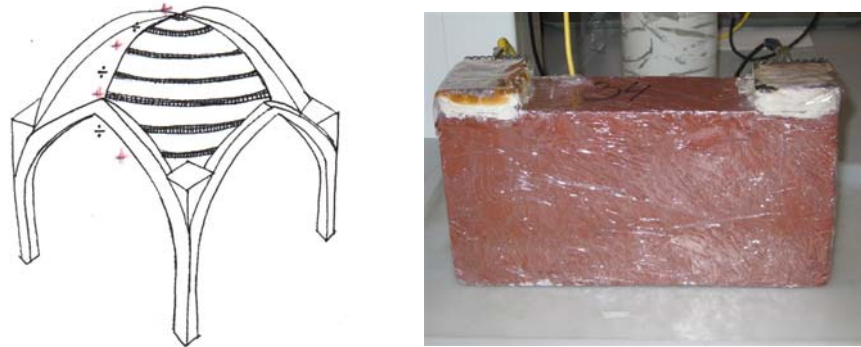


Figure 2. The left figure illustrates how the electrodes are thought to be placed on a church vault (solely on top of the vault) and the right picture shows the laboratory setup where the electrodes likewise solely are placed on the top.

4.3 Sampling Description

To make a diagnosis of the salt contamination in an existing building in Denmark, 10 mm (diameter) drilling powder samples are taken. As this method is used for existing buildings it is also used in the laboratory experiments to make them as comparable as possible with the real conditions. The size of 10 mm is a compromise to obtain representative results for both water and ion contents and still minimizes the size of the drilling hole. Drilling samples from church vaults were made with 6 mm drill to further minimize the holes [Larsen, 1999].

In total 9 drilling samples were taken from each brick in order to investigate the chloride removal. The brick was divided into 3 equal pieces both vertically and horizontally and is shown in Figure 3.

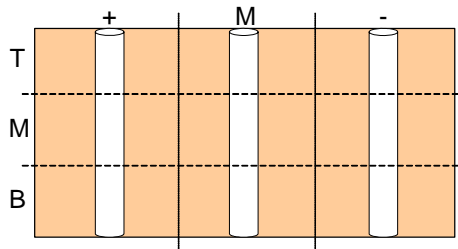


Figure 3. Sampling. Each brick was divided into 3 pieces both horizontally and vertically. The upper third closest to the electrodes is called top piece and the brick pieces just below the positive electrode is called + e.g. upper left piece is called +T.

4.4 Analytical

The concentrations of Cl^- and Na , were measured after extraction in distilled water. The extractions were made with 5 g dry brick powder and 12.5 mL distilled water and 10 g dry clay powder into 25 mL distilled water. The suspensions were agitated for 24 hours without air supply since this gave the most robust and reproducible values [Rörig-Dalgaard & Ottosen, 2008] and pH was measured with a pH meter directly in the suspensions. The chloride content was measured by a titrator (Metrohm 716 DMS Titrino).

4.5 Experimental overview

To assess expected improvement by addition of buffer at the electrodes on the salt extraction effect and extend of pH changes or stability, experiments with the basis poultice (kaolin clay and distilled water) and the newly developed poultices were carried out and compared. The experiments were named after the clay mixture and duration (e.g. CK 2 is carried out with carbonate as buffer compound at the anode and pure kaolin at the cathode and the experiment had duration of 2 weeks). A constant current of 40 mA was applied. The initial chloride content was 1.0 wt%.

Table 2. Experimental overview.

| Experiment | Duration [weeks] | Anode clay [buffer addition] | Cathode clay [buffer addition] |
|------------|------------------|------------------------------|--------------------------------|
| KK 3 | 3 | - | - |
| KK 4 | 4 | - | - |
| CK 2 | 2 | Carbonate | - |
| CK 4 | 4 | Carbonate | - |
| CA 2 | 2 | Carbonate | Acetic acid |
| CA 4 | 4 | Carbonate | Acetic acid |
| CA 6 | 6 | Carbonate | Acetic acid |

5. Results and discussion

The obtained results are evaluated on pH stability (section 5.1-5.3), extracted chloride from the brick into the poultice both as a function of time and accumulation throughout the experiment (section 5.4) and remaining chloride concentration in the brick after ended experiment (section 5.5).

5.1 Basic poultice at the anode and cathode – clarifying experiment

The pH changes were investigated by comparing the initial pH in the brick 8.6 +/- 0.1 and the pH after ended experiment.

An experiment with 1.0 wt% chloride was initiated. After 4 weeks application of the constant current of 40 mA the maximum voltage of the power supply was reached (136V) resulting in reduced current strength and the current had decreased from 40 mA to 4 mA. At the end of the experiment pH was measured in the drilling samples and the results are shown in figure 4a. The pH in the brick closest to the anode (T+) decreased to below 4 and pH in the brick closest to the cathode (T-) increased to 12. Such significant pH changes are unacceptable when the method is applied to cultural heritage. In all samples of the whole setup 8 out of 9 samples showed significant and unacceptable pH changes from neutral pH values 6-9 to pH below 4 and pH above 11.

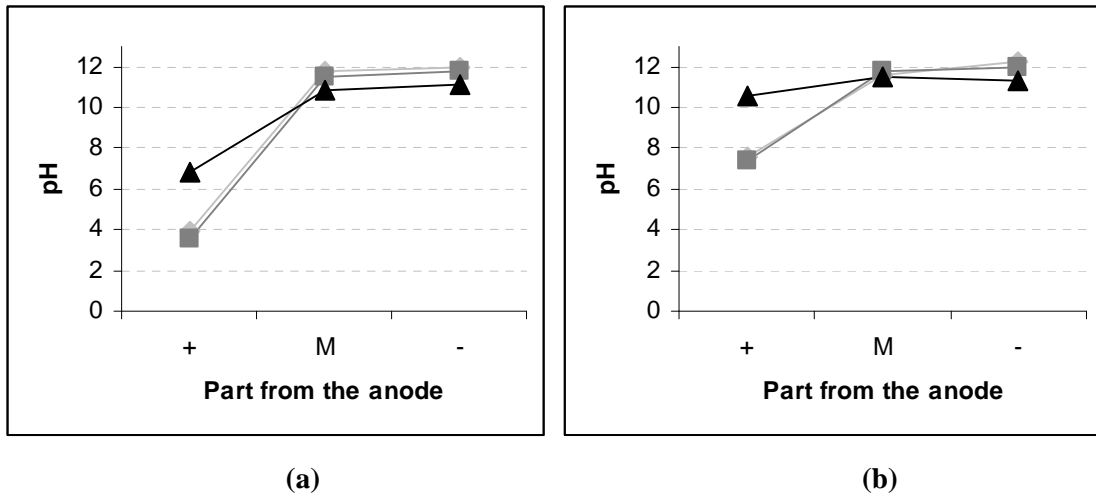


Figure 4. ♦ The upper 5 cm, top ■ the middle 5 cm ▲ and the lowest 5 cm, bottom (a). Extend of pH changes in series KK4 with no added buffering capacity at the electrodes.(b) Extend of pH changes in series CK4 with added buffering capacity at the anode. The initial pH was 8.6 +/- 0.1.

5.2 pH control solely at the anode

In the clarifying experiments (section 5.1), the need of pH control was pointed out. Acid neutralization by natural carbonate content in brick work clay has previously been used with success in pilot scale [Ottosen & Rörig-Dalgaard, 2006], and in experiments CK 2 and CK 4 it was tested whether the extreme and damaging pH changes could be avoided only by use of acid neutralization in the poultice at the anode. The exact amount of carbonate was calculated for the acid neutralization and the experiments carried out. After 4 weeks the resistivity increased significantly (136.1 V by 23 mA) and the experiment was ended. pH was measured in the brick powder and shown in figure 4b. Contrary to experiment KK 4, a neutral and non problematic pH was measured in the 10 upper cm closest to the anode (pH 7.4-7.6). Though, the base produced at the cathode had spread from the cathode to more than 2/3 of the brick and resulted in very high pH values (11.5-12.3). The need for pH control at the cathode was therefore obvious.

5.3 pH control at both anode and cathode

Experiment CA 2, CA 4 and CA 6 was carried out with pH control at both the anode and cathode. The exact amount of carbonate and acetic acid was calculated on basis of duration and current strength (consumed coulomb) and added to the kaolin clay and distilled water mixture. The experiment that lasted 6 weeks was ended as only very little chloride was left in the brick (0.003 wt % in average from all the 9 taken samples).

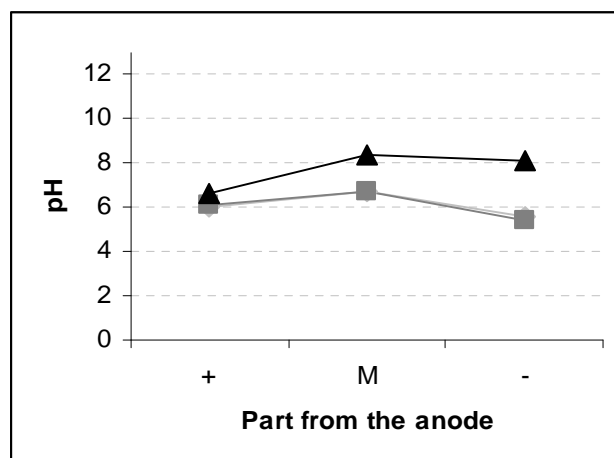


Figure 5. ♦ The upper 5 cm, top ■ the middle 5 cm ▲ and the lowest 5 cm, bottom. pH in the substrate after ended experiment CA 6 (pH control at both anode and cathode).

The pH values in the brick (CA 6) were measured, see figure 5. It was possible to avoid the extreme pH changes of the brick until satisfying desalination was obtained by use of buffer components in the poultice. Meanwhile some changes in the brick pH occur from the original pH of 8.6 to pH 6 closest to the anode and pH 5.4 closest to the anode. The measured pH values are though not expected to cause damage to brick and mortars and the pH changes are least in the bottom where the murals are. If the pHs decrease to 5.4 shows to be problematic, further improvement can be made, e.g. introduction of a two or three layered buffer poultice to reduce diffusion from the acetic acid clay into the brick. Comparison of the three experimental rows showed the necessity of pH control at both the anode and cathode to avoid extreme pH changes in the brick.

5.4 Extracted chloride

The poultice was changed once a week and the chloride content measured. To clarify changes in extracted chloride as a function of duration and thereby changes in efficiency during the salt extraction the measured chloride content was converted into extracted chloride per day. The average of the extracted chloride within the same brick (KK, CK, CA) is shown in figure 6 for the series.

The experiments with pure kaolin clay poultice at the anode and cathode (KK experiments), ends after 4 weeks as the voltage, by constant current, increase to the maximum of the power supply. Relatively little chloride is transported out in the poultice from where it can be removed. According to the theory H^+ ions will be transported instead of Na^+ ions when present and OH^- ions instead of Cl^- when present due to the exceptionally high ionic mobility of H^+ and OH^- .

Also in the experiment with carbonate as buffer material in the anode poultice and pure kaolin clay as cathode poultice (CK experiments) the experiment ends after 4 weeks as the voltage had increased to the maximum of the power supply. That the duration until high resistance is similar in the KK and CK experiments indicates that the increasing resistance mainly occurs next to the cathode. The chloride extraction improves considerably, though the performance of the desalination process is unstable and ends before satisfying desalination is obtained.

Only in the experiment with carbonate buffer poultice at the anode and acetic acid as buffer component in the poultice at the cathode the desalination is ongoing after 6 weeks were the chloride content was measured to 0.003 wt% in average and the experiment was stopped as the obtained chloride content was well below the threshold value in ÖNORM 3355-1. Increasing voltage was measured at the end of the experiments and indicates significant decrease in the total ion content. A stable desalination performance is obtained even at very low ionic contents and only a relative minor unproblematic voltage increase was seen contrary the other experiments (the initial voltage of 8 V in experiment CA6 increased to 37V at the end of the experiment).

The transport number is determined by:

$$t_{Cl^-} = \frac{Q_{Cl^-}}{Q_{total}}$$

Where the calculation of Q_{Cl^-} is based on the measured chloride content in the poultice, which is converted to number of chloride ions, and finally converted to current carried by this actual amount of chloride ions.

Q_{total} is the total current from the power supply in the given period. The calculated transport numbers for the series KK, CK, CA are shown in figure 6b. The transport number is low in the KK series (0.03-0.1), in series CK high in the first 3 weeks (0.55-0.69) and then significantly decreasing after 4 weeks were the experiment was ended. Whereas in series CA high transport number was maintained until almost complete desalination after 6 weeks. These transport numbers suggests that in the series KK even after one week the current is mainly transporting H^+ instead of Cl^- . In the CK series the Cl^- transport is efficient. However, between week 3 and 4 the voltage increases significant (from 20V to 132V) which ends the experiment, probably due to pore clogging by produced $Ca(OH)_2$. Only in the CA series a high transport number is maintained until no more chloride is to be transported. Cl^- transport number is up to 0.69. Since the mobility of Cl^- ($7.91 \cdot 10^{-8} m^2s^{-1}V^{-1}$) is higher than for Na^+ ($7.91 \cdot 10^{-8} m^2s^{-1}V^{-1}$) [Atkins, 1994] a transport coefficient above 0.5 was expected in case of an efficient system.

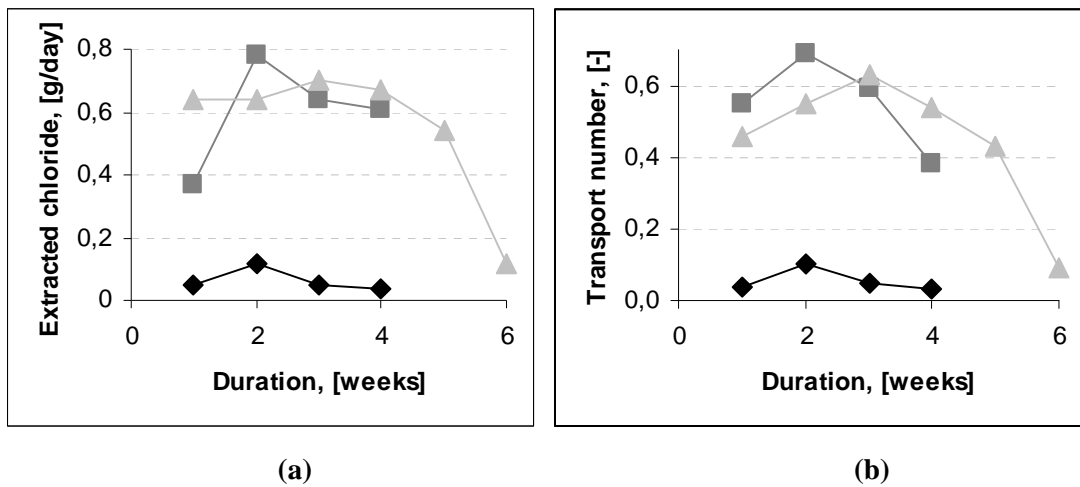


Figure 6 (a). Desalination effect as chloride extracted per day with and without the new poultices. (b) Chlorides transport number. ♦ Pure kaolin clay at both the anode and cathode ■ Carbonate clay at the anode and pure Kaolin clay at the cathode ▲ Carbonate clay at the anode and Acetic acid clay at the cathode.

In figure 7 is the extracted chloride summed up over the series duration time.

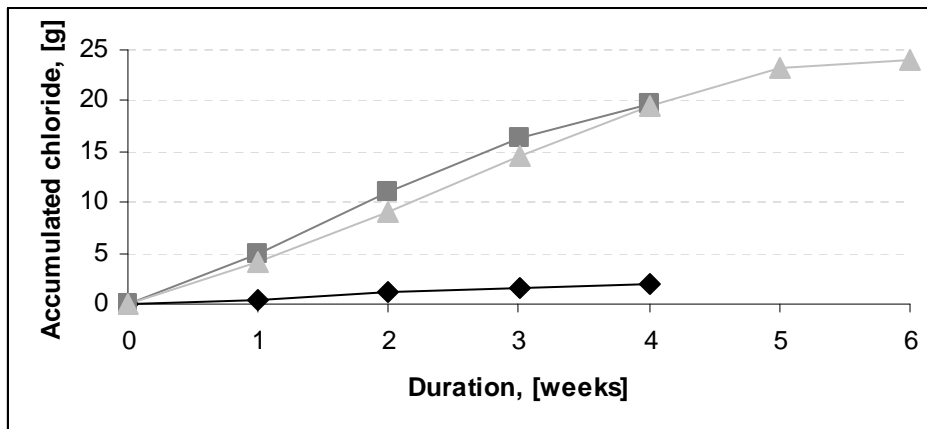


Figure 7. Accumulated chloride content in the poultice throughout the whole experiment duration. For the series: ♦ KK ■ CK ▲ CA.

With the basis poultice, only very little chloride was extracted (1.9 g chloride). Addition of buffer compounds to the anode poultice leads to a considerable higher total chloride extraction (19.6 g chloride) but the desalination process ends before the threshold value of 0.03 wt% chloride is obtained, see table 3 (see also figure 10 for the obtained chloride content). Only by use of buffer compounds in both anode and cathode poultice satisfying chloride reduction in the setup is obtained (24 g chloride extracted).

Table 3. Chloride concentration, water content and pH in the brick after ended treatment. The initial content of : water was 12.6 +/- 0.4 wt%, of chloride 1.0 wt% and the initial pH 8.6

| Experiment | Remaining chloride concentration [wt%] | Final water content [wt%] | pH at the anode/cathode |
|------------|--|---------------------------|-------------------------|
| KK 4 | 0.18 +/- 0.07 | 2.9 +/- 0.9 | 3.9/12.0 |
| CK 4 | 0.15 +/- 0.16 | 2.7 +/- 1.0 | 7.6/12.3 |
| CA 6 | 0.003 +/- 0.01 | 4.0 +/- 0.6 | 6.0/5.6 |

5.5 Obtained chloride content

The remaining chloride contents in the brick after ended experiments are shown in figure 8.

The average chloride content after ended KK4 experiment was 0.18 wt%, 0.15 wt% in the CK4 experiment, and 0.004 wt% in the CA6 experiment, see table 3.

Chloride from the inner part of the brick may have been transported towards the surfaces as a part of the evaporation process and as KK4 and CK4 were only ongoing for 4 weeks a higher evaporation could have occurred in comparison to CA6 which was ongoing for 6 weeks. Though, this is not the case as seen in table 3 since the highest water content was present in CA and the remaining measured chloride content seems therefore to be a result of differences in desalination possibilities with the different poultices.

The remaining chloride content for KK4 (figure 8) was lower than expected on basis of the measured accumulated chloride in the poultice (figure 7). This is assumed to be caused by precipitation of ions to salts at the high present pH (10-12). In consistence with this a tendency for more effluences were seen at the surface of KK4.

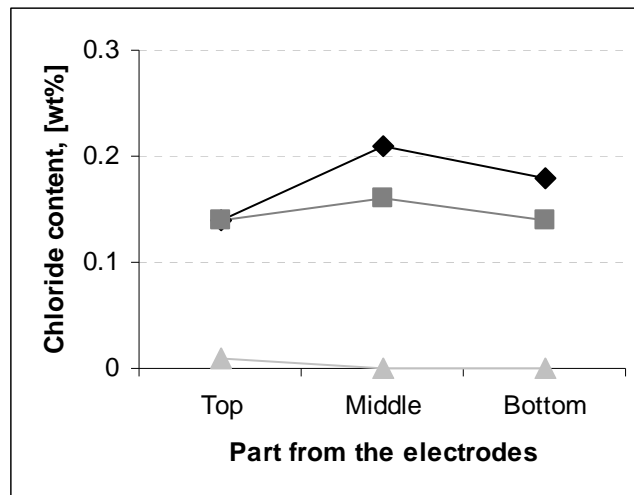


Figure 8. Remaining chloride content in the brick after ended experiment of: ◆ KK4 ■ CK4 ▲ CA6.

6. Conclusion

In this paper the desalination effect by use of electromigration, pH changes and the necessity of developing new electrode units were in focus.

A clarifying experiment pointed the need of pH control out to prevent pH changes in the brick and to optimize the desalination process. In the clarifying experiment no precautions were taken against the acid and base produced at the electrodes and only very little salt was extracted from the brick before the resistivity between the electrodes increased to the maximum of the power supply and the experiment was subsequently stopped.

New poultices were developed for neutralization of the pH changes at the electrodes. Previous work has shown a positive effect of natural carbonate rich clay to hinder the acid from the anode in entering the brick. The new development in this paper was the calculation of actual needed neutralization effect (dependent of current strength and duration) and addition of needed carbonate to the poultice to obtain sufficient buffer effect. Likewise use of buffer compound (acetic acid) for neutralization of the produced base at the cathode was a new development in this paper, and carried out by preliminary calculation of the neutralization need and subsequent addition to the poultice. The development of the poultices at the electrodes resulted in maintaining a neutral pH in the brick and desalination from problematic chloride content to very low and completely unproblematic chloride content. These new developments are through to be very promising is regarded an important step towards implementation of the method and the basis for a patent application [Rörig-Dalgaard & Ottosen, 2008 B].

Acknowledgements

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Desalination of a wall section with murals by electromigration

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Abstract

Presence of salts is a threat against the preservation of murals. In the present work, the application of an electric DC field (an electrokinetic method) was investigated for the removal of NaCl from a wall section with murals. An applied current of 2.9 mA/cm was used, and the duration of the treatment was two weeks. Both chloride reduction in the wall section and accumulation of the extracted chloride in a removable poultice between the wall section and the electrodes were shown. The removal efficiency was high in some parts of the wall but low in other parts, dependent on the ease of moistening of the actual part of the wall section.

The pH was measured in the wall section before and after treatment and no changes were observed. Pigments in the murals have very low solubility at neutral pH, but some pigments have increased solubility in extreme acidic or alkali environments. Since only dissolved pigments can be transported in an electric field, no changes in the pigments were expected after treatment was ended. The pH did not change and no changes were visually observed after the electrokinetic treatment.

Keywords

Electromigration, desalination, wall section, pigments solubility, pH, pilot plant desalination

1. Introduction

Increased deterioration of murals on salt loaded brick masonry church vaults has been observed by conservators from the Danish National Museum within the last decades. In contrast to medieval times, churches are heated for services (during the winter) and

unheated for the rest of the week, resulting in a dissolution-crystallization cycle just within one week [Larsen, 1999].

In the present work, the use of electromigration is proposed as a working principle for the removal of NaCl from the masonry vault. The use of an electric DC field across a 0.5 cm brick has previously shown an increased ion velocity in short experiments (up to 50 hours) [Buchwald, 1997]. In the authors previous work, experiments with an optimized laboratory setup with a single brick showed good results and a dangerously high chloride content of 1.0 wt% (added as NaCl) was reduced to 0.004 wt% [Rörig-Dalgaard & Ottosen, 2008]. This is well below the unproblematic threshold value of 0.03 wt% given in ÖNORM 3355-1. In the present paper the aim was to evaluate the method on a larger laboratory scale experiment carried out on a wall section. Furthermore, an important point of the investigation was to evaluate the influence of the electric field on the mural's pigments.

2. An applied DC field and pigments

2.1 The electric field

Salts dissolve totally in water into positive and negative ions until the point of saturation. By application of an electric DC field a positive and a negative electrode is established and the ions in the solution will be attracted to the electrode of opposite charge, and the ions will move in the electric field. This phenomenon is termed electromigration, figure 1.

By the use of electromigration a controlled ion transport is obtained in wet, porous materials such as bricks. When transporting the damaging ions out of the church vaults into an accumulating layer surrounding the electrodes, the ions can be removed after the treatment is completed together with the accumulating layer and the contamination is removed.

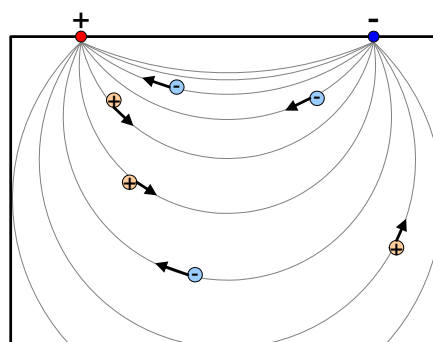


Figure 1. Principal sketch of potential and current distribution in a vertical plane along the line of electrodes with ion migration. Freely after (van Nostrand 1966)

2.2 Electrode reactions

An electric circuit in a wet brick is maintained by electrons in the electrodes, which are transformed through electrode reactions to ions in the pore solution and visa versa.

Among others, these electrode reactions result in the production of acid at the anode ($\frac{1}{2} \text{H}_2\text{O} (\text{aq}) \rightarrow \text{H}^+ + \frac{1}{4} \text{O}_2(\text{g}) + \text{e}^-$) and base at the cathode ($\text{H}_2\text{O} (\text{aq}) + \text{e}^- \rightarrow \text{OH}^- + \frac{1}{2} \text{H}_2 (\text{g})$) [Acar, 1993]. If no precautions are taken for neutralization of the acid and base produced at the electrodes, pH of the material and thereby the material composition of the brick and mortar will change to some extent. Meanwhile, laboratory experiments have shown that it is possible to limit the pH changes to minor changes [Rörig-Dalgaard & Ottosen, 2008]. The metallic electrodes are placed in a layer that neutralize the acid and base at the anode and cathode, respectively.

2.3 Pigments solubility

Only dissolved pigments are in risk of transport in an electric DC field.

In St Gabriel's Chapel, Canterbury Cathedral in England, identification of pigments was carried out and found to be: natural ultramarine ($\text{Na}_{8-10}\cdot\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$), malachite ($\text{CuCO}_3\cdot\text{Cu}[\text{OH}]_2$), cinnabar (HgS), red lead (Pb_3O_4), red earth (Fe_2O_3), yellow earth ($\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$), lead white ($2\text{PbCO}_3\cdot\text{Pb}[\text{OH}]_2$), lime white (CaCO_3) and carbon black (C) [Cather, 1994]. The solubility of some of these pigments is listed in table 1 [Robinson, 1988].

Among the solubility data in table 1, calcite present in the lime layer as ground layer for the mural has the highest solubility and will accordingly dissolve before $\text{CuCO}_3 > \text{PbCO}_3 > \text{HgS}$. However, calcite only dissolves to a very small extent at neutral pH, and dissolution of the used pigments is therefore expected to be very unlikely as long as pH changes are avoided. The wall section used in the present paper was made 14 years ago, and unfortunately knowledge of the exact pigments used was not available.

| | Solubility products by 25°C |
|-----------------|-----------------------------|
| CaCO_3 | $4.8\cdot 10^{-9}$ |
| CuCO_3 | $1.37\cdot 10^{-10}$ |
| HgS | $2\cdot 10^{-59}$ |
| PbCO_3 | $1.5\cdot 10^{-13}$ |

Table 1. Solubility of some pigments. From [Robinson, 1988]

2.4 pH dependent solubility of pigments

The solubility of the pigments is very dependent on pH. The different pigments used for Danish murals have significantly different chemical properties, and the solubility of some pigments are pH dependent (e.g. Cr_2O_3 – real chromium green), some dissolve in acid ($\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ -azurit-the most applied blue color in Denmark), some dissolve in base (As_2S_3 Auripigment traditional yellow color in Denmark) and some dissolve in both acid and base (CoO, nZnO - cobaltgren) [Christensen, 1991]. This again underlines the importance of avoiding pH changes in the layer of the murals during the electrokinetic treatment.

3. Experimental

3.1 Wall section with murals for the investigation

The wall section used in the present work was inherited from the Danish National Museum, where it was made in the summer 1994. Preparation of the wall section followed in several steps. The masonry consists of Falkenløwe bricks and mortar mixed from Rødving Kulekalk and Kronhøj mortarsand (particle-sizes 0-5.0 mm) in the ratio 1:3. The painting was made by a conservator from the Danish National Museum's murals conservation department. The wall section is shown in figure 2. After carbonization of the lime mortar (approximately one year), a sodium chloride solution

was sprayed on the left half of the wall section. The right part was left untreated for reference purpose. The sodium chloride solution was sprayed on from the back of the wall with a pollinator and the wall section was stored indoors for 14 years.

Peeling of the lime layer with painting occurred as expected due to ion transport towards the surface in the salt contaminated part followed by salt precipitation (the largest area inside the ring in figure 2).



Figure 2. The wall section. Severe salt damage inside the red ring.

3.2 Sampling description

For determination of the initial salt content, drilling samples (6mm) were made both from the salt and the non salt contaminated part before and after treatment. A hole was drilled through the entire depth, in the three intervals from the front side of the mural: 0-5 cm (termed bottom), 5-10 cm (termed middle) and 10-14 cm (termed top). Samples were taken both close to the edge of the wall section (-2, 1, (3)) and from the inner part (-1, 2), see figure 3. The drilling samples before and after treatment were made close to each other. Furthermore, spot checks of the poultice from the electrodes were made by extraction of 5 g from the poultice for each 9 cm.

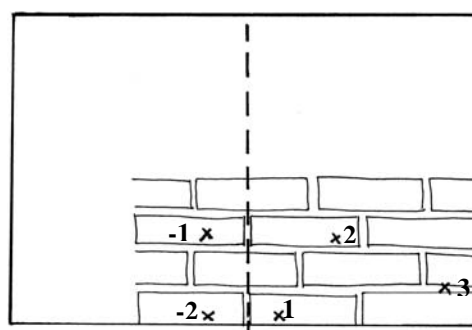


Figure 3. Sketch of the wall section, regarded from above. The left part is supposed to be noncontaminated, whereas the right part is salt contaminated.

3.3 Analytical

Water content in the brick powder was determined after drying of the samples at 105°C until equilibrium (obtained after approximately 24 hours).

In relation to electromigration only soluble ions are of interest. The supplied and dominating ions Cl^- and Na^+ are soluble too, and extractions with 5.00 g dry brick powder in 12.50 mL distilled water for 24 hours undisrupted agitation was carried out (this procedure has been tested and found suitable in connection with bricks [Rörig-Dalgaard & Ottosen, 2008 B]). The pH was measured with electrodes directly in the suspension after settling for 5 minutes (or until a clear liquid came into existence). After mixing 2 ml of the suspension with 35 ml distilled water and 1 ml 1M HNO_3 the chloride content was measured with a titrator (Metrohm 716 DMS Titrino).

3.4 Laboratory experiments

To simulate a church vault the wall section was rotated to horizontal position and placed on metal trestle (with plastic covered wood in between to avoid any electric contact), figure 4. The rotation was made manually, and unfortunately resulted in reduced adhesion between the mortar and bricks in the whole wall section.

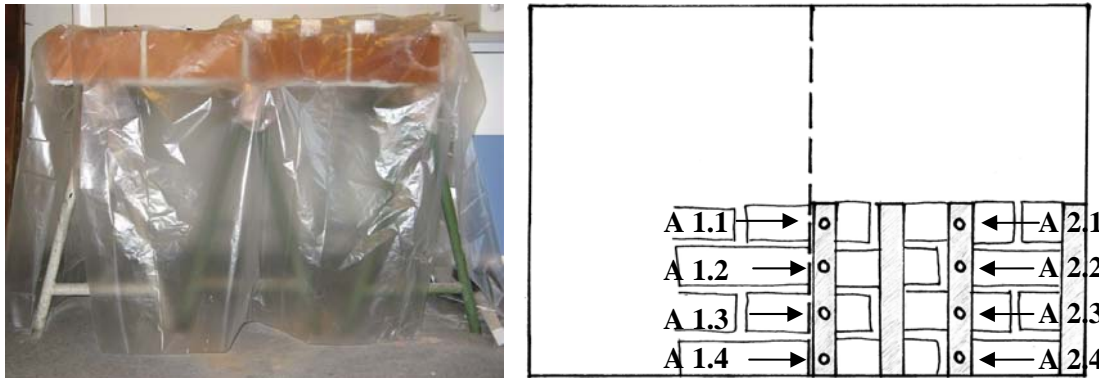


Figure 4. Left: the whole wall section and the plastic covering to minimize evaporation. Right: Numbering of the spot checks from the poultice taken above each brick (e.g. A 1.1 means anode setup one, spot check number one).

In a vault, the sodium content exists either as dissolved ions or nucleated salts. Since the wall section was stored indoor for 14 years, the present sodium chloride was expected to exist as nucleated salts. Dissolution of the salts was necessary before electrokinetic treatment. Friese and Protz [2002] reported a possible electric circuit in brick masonry with at a water content of 3-4 wt%. Larsen [1999] only added water to a church vault to an assumed content of 2.5 wt% in connection with accelerated ion transport with a sacrificial layer and controlled climate (climate chamber). To protect the mural from peeling, no dissolution-crystallization should take place on the murals surface, and the water was therefore sprayed on from the mural's side (from below). However, the water uptake from below was very slow (maybe due to limited contact between lime layer and brick masonry), and for this reason the main part of the water was in contrast to the original intension added from the top. During the experiment, the evaporation rate could be assessed on the basis of the voltage drop, since a connection has been found between voltage drop and water content in experiments with single bricks (not shown). When the water content was assessed to be too low, additional water was sprayed on the surface. The water was only sprayed on the salt contaminated part of the wall section.

The experiment included two sets of parallel working electrodes. A current strength of 108 mA was applied through electrodes with the length of 38 cm (corresponding to 2.85 mA/cm electrode). The anodes were 3 cm wide oxide coated titanium meshes and the cathodes 5.5 cm wide stainless steel meshes. The distance between anode 1 and cathode 1 was 10.4 cm whereas the distance was 20.8 cm between anode 2 and cathode 2, where the 20.8 cm corresponds to the previously conducted laboratory experiments with single bricks [Rörig-Dalgaard & Ottosen, 2008]. The poultice was placed in rectangular forms (L: 38 cm × D: 5.5 cm × H: 3.5 cm) to ensure the right amount of poultice and ease in the calculation of extracted chloride. The forms were placed perpendicular to the length of the bricks and below the full length of the electrodes.

4. Results and discussion

During the electrokinetic treatment, the desalination effect was evaluated by measuring chloride content in the removed poultice. Drilling samples from the masonry were made both prior to and after the experiment to investigate changes in chloride content and pH in the wall section.

4.1 Chloride extraction

The desalination effect of the electrokinetic method must be evaluated by the relation between the amount of extracted damaging ions and the total charge transfer due to the current, as well as the final concentration remaining in the masonry. The poultices at anode 1 and 2 were divided into four segments each. A spot check was made from the middle of these four segments and the numbering is shown in figure 4, right. The chloride concentration was measured in the poultice and converted to extracted mass (figure 5) on basis of the total mass of the segment.

Significant variations in extracted chloride for the different positions (bricks) were measured. In general, the chloride extraction was smaller in electrode setup 1 than 2. In electrode setup 1, only relatively small amounts of chloride were extracted. In electrode setup 2, the extracted chloride varies between little to relatively high. However, it must be noticed that the smaller distance between the first set of electrodes than between the second set results in a smaller possible chloride extraction (smaller area with chloride contamination), but even taking this into account the electrode setup 2 is more efficient.

In position 1 (corresponding to extractions measured in A 1.4) the average chloride content was reduced from 0.16 wt% to 0.06 wt%. A total of 0.45 g chloride was found in the poultice in position A1.4, corresponding to a change in an entire brick of 0.009 wt%. In position 3 (corresponding to extractions measured in A 2.4), the chloride content increased after treatment from initial 0.11 wt% to 0.17 wt%, and at the same time a chloride extraction in the clay was measured as 3.5 g, corresponding to a change in the chloride content in one brick of 0.07 wt%. In total, approximately 8 g chloride was extracted during the 2 weeks treatment for both electrode setups. In previous single brick experiments under ideal conditions (capillary saturated, 1.0 wt% chloride) [Rörig-Dalgaard & Ottosen, 2008], electrokinetic extraction between 3.8 and 5.6 g chloride was obtained per brick with the same current consumption. Comparison of the extracted chloride per brick in the present investigation (figure 5) with the single brick experiments, therefore, indicates that the principle of electrokinetic extraction might be efficient in larger scale, too, provided sufficient wetting will occur.

Even though the electrodes were placed perpendicular to each brick, corresponding to previous single brick experiments, current distribution and evaluation could not be made for each brick, but as a whole. This is most probably a consequence of the fact that salt contamination creates an interconnected system in the whole area and not separate systems. In interconnected systems the electric field lines are most intense in the places with highest conductivity independent of material or borders.

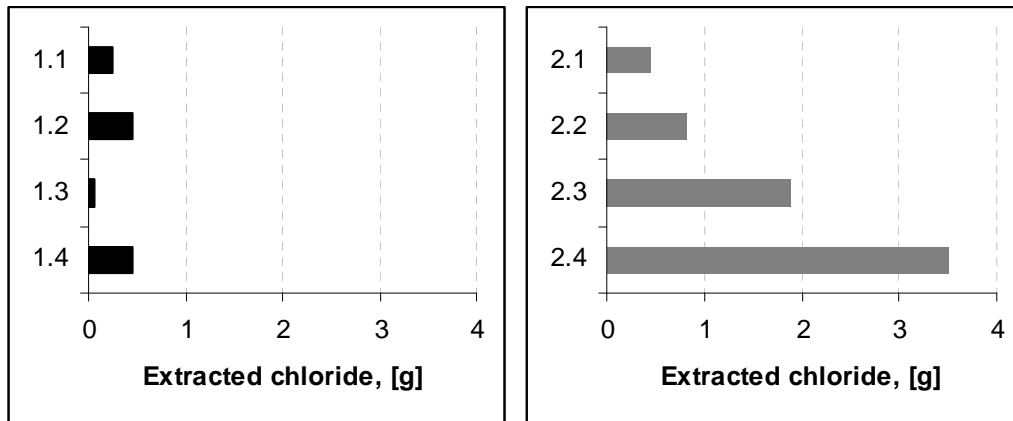


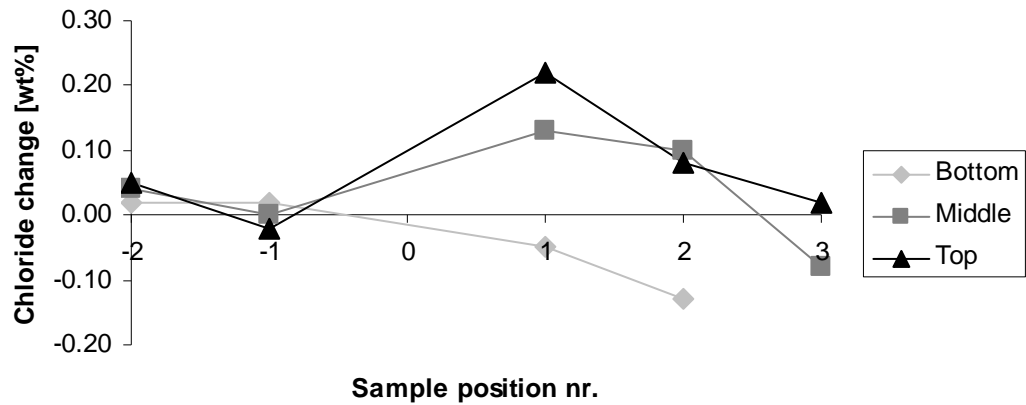
Figure 5. Accumulated chloride in the poultice by anode set 1 and 2 in each of 4 positions.

4.2 Chloride content in the wall section

The chloride content was measured in the wall section before and after treatment. Low concentrations were expected in the sample positions -2 and -1 (sampled in the area of the wall section where no salts were sprayed on), whereas high salt contamination was expected in the sample positions 1, 2 and 3, since the sodium chloride solution was sprayed on this half, see figure 6.

The chloride concentration before treatment varied from below 0.05 wt% to 0.35 wt%. The norm [ÖNORM B 3355-1] suggests a limit of 0.10 wt% as potentially damaging, whereas chloride content between 0.03 and 0.1 should be evaluated individually. The chloride concentration in position -2 before treatment was, contrary to the predictions, at a damaging level (0.15 wt% +/- 0.11), whereas the chloride concentration in position -1 was found to be unproblematic (0.01 wt% +/- 0.004). All initially measured chloride concentrations, in all depths at position 1, 2 and 3 were problematic according to the norm.

In position -2, a small reduction in chloride concentration was measured for all three samples: top, medium and bottom. These samples were taken close to the edge of the wall section, where moistening was easier and reduction in the chloride concentration in this area was most likely caused by water and ion transport towards the surfaces due to evaporation, since the electric DC field was not applied above this area. In position -1, no significant changes were observed, as expected, since the electric DC field was also not applied above this area. In position 1, almost complete chloride removal was obtained for the upper 2/3 (10 cm). In position 3, a minor reduction in chloride concentration was obtained in the upper 1/3. In position 2, no general reduction in chloride concentration was measured, only a redistribution, where the concentration was increased in some places and decreased in others.



| | Sample position nr. | | | | |
|-------------------|---------------------|------|------|------|------|
| | -2 | -1 | 1 | 2 | 3 |
| Bottom (B) | 0.04 | 0.02 | 0.12 | 0.35 | (-) |
| Bottom (A) | 0.02 | 0.00 | 0.17 | 0.48 | 0.25 |
| Middle (B) | 0.15 | 0.01 | 0.13 | 0.16 | 0.11 |
| Middle (A) | 0.11 | 0.01 | 0.00 | 0.06 | 0.19 |
| Top (B) | 0.25 | 0.02 | 0.22 | 0.13 | 0.10 |
| Top (A) | 0.20 | 0.04 | 0.00 | 0.05 | 0.08 |

Figure 6. Measured chloride contents before (B) treatment and after (A) treatment are all shown in the table and in the figure as changes in wt%. A decrease in chloride content between before and after treatment is shown as a positive change in the figure. Sample position below zero are in the salt free area and above zero from the salt contaminated area. The drilling samples before and after treatment were made close to each other. (-) not measured.

When the wall dried again after the experiment, the degree of ion transport was clearly visible (figure 7a), since efflorescence developed in the areas with no reduction in chloride concentration. This corresponds to the transport pattern seen in single bricks experiments figure 7b. The measured reduction in chloride concentration at the positions 1 and 3 corresponds well to the visual ion transport seen in figure 7a.

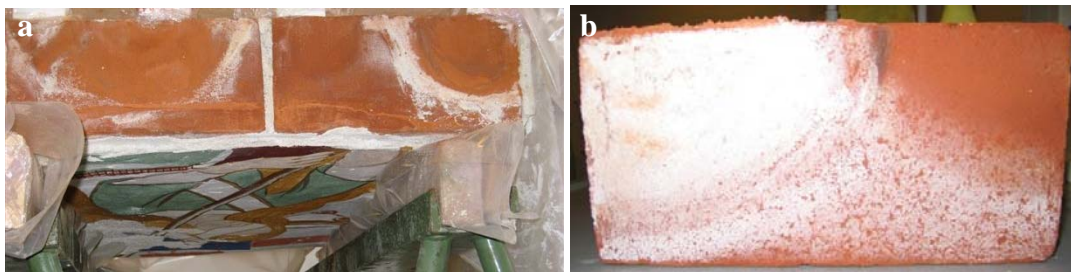


Figure 7 (a) Picture of ion movement after 2 weeks treatment crystallized as salts after evaporation, corresponding to the measured values in figure 6. (b) Similar visible salts on a single brick.

The most pronounced reduction in chloride concentrations were obtained in sample position 1 and 3, which were situated closest to the edge, where wetting was more efficient, compared to sample position 2 taken from the middle of the wall section. This indicates that the electrokinetic methods efficiency was dependent of the moisture supply.

Comparison of the extracted chloride amount in the poultice and the reduction in chloride concentration in the wall section shows that evaluation of both is necessary to obtain a more reliable picture of the total chloride removal.

4.3 The pH in the wall after treatment

In a previous investigation with electrokinetic treatment of single bricks, it was shown that by using a specially developed poultice at the electrodes it was possible to limit the pH changes to minor changes [Rörig-Dalgaard & Ottosen, 2008]. To ensure and prove pH stability in the wall section after application of the electrokinetic method, the pH was also measured in the drilling samples both before and after treatment (figure 8).

Comparison of the pH before and after treatment shows no systematic differences. An average of the pH before treatment was 9.3 +/- 1.4 (between 8.2-12.5) and after treatment 9.1 +/- 1.1 (between 7.5-12.0). Additionally, no significant difference was measured between the area without applied current (-2,-1) and with applied current (1, 2, 3).

As there was no significant change in pH of the wall, the pH in the painted layer remained unchanged, and there was no solubilization of the pigments. Correspondingly, no change in the murals surface was observed after the treatment.

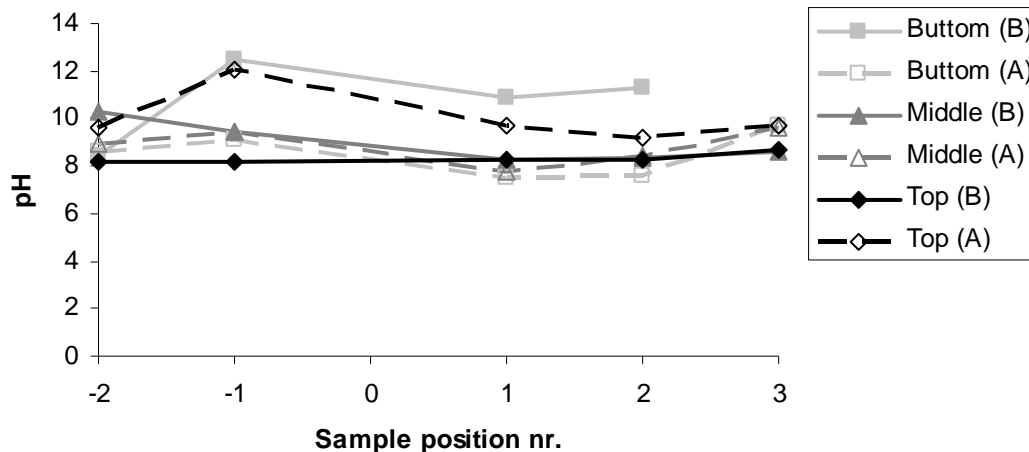


Figure 8. pH measurements at position: -2, -1, 1, 2, 3 before (B) and after (A) treatment. Sample positions below zero are from the area without an applied electric DC field contrary the sample positions above zero.

5. Conclusion

In this first electrokinetic treatment of a wall section with paintings on pilot scale (2 weeks duration), electromigration seemed to be a powerful transport mechanism for the areas where wetting was unproblematic both in terms of reduction of the chloride concentration in the wall and the increased concentration of chloride in the poultice at

the electrodes. For the areas where wetting was less efficient, a lower efficiency was measured.

For an interconnected system, as this larger salt contaminated area of brick masonry, efficiency evaluation should not be made for single bricks, since ion transport occurs across bricks borders. Instead, evaluation must be carried out on bricks from the whole area and/or the extracted salts.

The solubility of pigments at slightly alkaline pH is exceptionally low, and only in the case of extreme acidic or alkaline environment the solubility increases for some pigments. Since no pH changes were found in any of the brick samples as a consequence of the electric field, no pigments changes were expected in the lime layer with the pigments, and corresponding to this, no changes on the mural's surface was observed during the treatment.

Improvement of the wetting process in future treatments will presumably result in equally satisfying chloride reductions on large scale as seen in previous single bricks experiments.

Acknowledgments

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Impact of gypsum formation on deterioration of on a painted monastery vault shown by SEM- EDX analysis

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Abstract

Salts deterioration effect has been studied for more than hundred years, but the mechanisms are still not fully understood and the existing models only partly describe the deterioration process. Most measurements for clarification of the deterioration process have been carried out at laboratory conditions. The present contribution aims to clarify the deterioration process that had occurred in the so-called Birdsroom in the Carmeliter Monastery (Vor Frue Monastery) in Helsingør, Denmark. Samples were taken from the masonry at the loft above the vault, at the upper surface of the vault itself and from repealed materials below the vault.

The investigations showed that the primary source for salt contaminant most likely was sodium chloride used for preservation of perishable food in ancient preservation. Meanwhile, in the most accepted theory for salt deterioration, crystallization pressure, does not justify sodium chloride induced damages.

Besides sodium chloride, sulfur was found at all fractures originating from the vault by element mapping with Energy Dispersive X-ray Spectroscopy (EDX) mappings and overlapping EDX mappings with calcium, oxygen and sulfur make probable that gypsum was the determining deterioration factor.

Keywords

Salt deterioration, painted vault, sulfate, chloride, sodium

1. Introduction

The state of 330 murals in Danish churches was investigated [www 2] and from these 33 had salt problems. According to this investigation, presence of salt are considered as the most serious threat against preservation of murals.

Presence and damage from salts is also well known in other countries, and [Sawdy & Price, 2005] described salt induced damage as a frequent problem in connection with conservation and the salts deteriorating effect is pronounced by wall paintings.

[Rodriguez-Navarro & Doehne, 1999] summarize several authors' recognition of salt weathering as one of the primary reasons for deterioration in connection with historic architecture. Within the recent years several European projects have been initiated with the aim of protecting the cultural heritage from salt deterioration e.g. [www3], [www4]. Extensive deterioration of the birds' room in Vor Frue Monastery, Helsingør, Denmark is unfortunately a fact, figure 1.



Figure 1. Extensive deterioration of the painted vault in the so-called Birds room in Vor Frue Monastery, Helsingør, Denmark. (Left) an overview (Right) a detail.

Presence of salts and the changes in RH during the year (the room is unheated) are considered the major cause for the deterioration. The present paper focuses on identifying which salts are precipitated in bricks and paintings.

Vor Frue Carmeliter Monastery with Sanct Mariæ Church, Helsingør, Denmark is one of the most well preserved monastery assets in northern Europe and was built between 1450-1500. The murals were painted around 1500 AD and uncovered in 1901-06 under the Danish renovation architect H.B. Storch. The murals decoration consists of red leaf parsley patterns and birds [www 1]. In the present paper the salt pollution source, ion movements within the vault and revealed layers were investigated in order to clarify the deterioration process.

2. Salt deterioration processes

The most accepted mechanism for salt induced deterioration describes the crystallization pressure as the determining deterioration factor. The crystallization of soluble salts in porous materials can generate pressures inside the pores sufficient to exceed the tensile strength and result in material damaged [La Iglesia et al., 1997]. Salt crystallization occurs when there is equilibrium between evaporation (moisture transition coefficient of the surface) and liquid transport towards the surfaces (moisture transport coefficient) [Snetlage & Wendler, 1997], [Lewin, 1978], [Lubelli et al., 2006b]. Snetlage & Wendler (1997) calculated by a numerical model the depth of this evaporation zone from the surface for natural stones with varying dense. They proved through experiments with a test wall the coherence between increasing dense and reduced evaporation zone depth and also coincident between evaporation zone and the brittle detachment zone.

The crystallization pressure is dependent on the specific crystals formed [La Iglesia et al., 1997]. However, the crystallization pressure connected to sodium chloride does not justify the observed deterioration in several case studies. Both material properties (pore size, mechanical strength, moisture transport behavior) and boundary conditions (moisture supply, salt load and distribution, environmental conditions) influences the decay pattern and extend. Sodium chloride related damages was shown to be caused by a mechanical interaction between salt and pore wall were RH changes (and thereby crystal changes) can lead to stresses on the pore wall in case of adhesion between material and salt [Lubelli, 2006]. Also [Scherer, 1999] relates the degree of deterioration to the surface properties of the porous material described by the contact angle between the crystal and pore walls. [Rodriguez-Navarro & Doehne, 1999] suggested differences in crystallization patterns between reduced deterioration by efflorescence with NaCl (crystallization at the material surface) and extensive deterioration by subflorescence with $\text{NaSO}_4 \cdot 10\text{H}_2\text{O}/\text{Na}_2\text{SO}_4$ (crystallization inside the material) as a determining parameter in agreement with their laboratory experiments. Winkler & Wilhelm (1970) also showed high dependence of relative humidity and temperature, by calculated maximum stressed under ideal conditions.

Snetlage & Wendler (1997) made laboratory experiments with clay-rich sandstone samples saturated with gypsum solution exposed to evaporation during approximately 170 days and found dots of gypsum below repealed surface material and concluded that gypsum was the reason for this deterioration.

The deliquesce point of all three calcium sulfates: gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) and anhydrite (CaSO_4) are close to 100% RH, though the solubility is strongly influenced by presence of other ions. The influence on the solubility of gypsum from more soluble salts e.g. NaCl was sketched Lubelli et al. (2004) and experimentally shown to increase the gypsum solubility with up to a factor three [Charola et al., 2007]. Also Larsen (2007) carried out simulations using the program RUNSALT and showed that presence of sodium chloride increases the solubility of calcium sulfate, this enable it to migrate and accumulate at the surface causing the deterioration. In the presence of NaCl the conversion of gypsum to anhydrite occurs when the deliquesce humidity of the second salt is exceeded. Gypsums increased solubility in comparison to the theoretical value has been observed at many sites e.g. [Zehnder, 1996], [Zehnder, 1993].

Gypsums low solubility seems to reduce the drying rate in the porous materials, resulting in gypsum accumulation in the evaporation front and pore clogging at the surface and inside the material (crypto crystallization). Crypto crystallization may

generate stress, termed crystallization pressure. Gypsums damaging effect is presumable caused by crystallization cycles within the porous materials. Dehydration of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) or anhydrite (CaSO_4) and rehydration may also contributes to the deterioration process [Charola et al., 2007].

3. Methods

The samples were visually studied through Environmental Scanning Electron Microscopy (ESEM), FEI QUANTA 200. Element screening and mapping within part-areas at different positions of each sample was carried out by Energy Dispersive Spectroscopy X-ray Microanalysis (EDX) to determine the elements in the salt crystals and quantitative distinguish between contents from the brick matrix and elements from the polluting salt.

Mappings by EDX covered small areas, 50-250 μm in length at the chosen magnifications and measurements at several positions of each sample were made to evaluate the possible generalization of the results found.

4. Sampling description

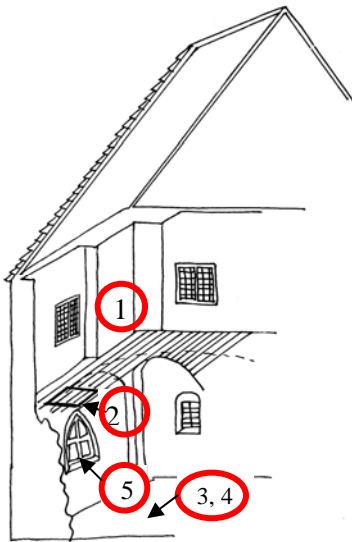


Figure 2. Sampling positions.

The history of structures is essential for the damage situation [Zehnder, 2006] and also the surroundings have a major impact on the structure [Zehnder, 2007]. Therefore were possible deterioration reasons and patterns taken into account when choosing the actual sample positions.

During sampling at the Carmeliter Monastery it was taken into account that specific and pure crystals would ease the analysis and interpretation of the result as described by [Zehnder, 2007]. Samples were taken with carbon tabs on a pin for the SEM-EDX investigations from the deteriorated surfaces inside the building. Both samples of effluence and repealed layers were taken to track the deterioration evolution above, on top of and below the deteriorated vault. The five places for sampling in the monastery are shown in figure 2.

1. Deteriorated bricks above the vault.
2. Efflorescence at the top of the vault (access through a hatch in the wooden floor).
3. A lime flake/layer (0.4 mm thick) found at the floor below the vault.
4. A lime piece (3.6 mm thick) found at the floor below the vault.
5. A lime piece found in a windowsill below the vault.

5. Salt content and distribution in the samples

5.1 Deteriorated bricks above the vault

Above the birds' room is a large loft. At this loft deterioration of the masonry is only pronounced in the south-west to north-west corner (figure 3) whereas the other masonry seems uninfected. The damages are located exactly above the birds' room.



Figure 4. Deteriorated corner above the birds room. (a) Direction south-west (b) Direction north-west.

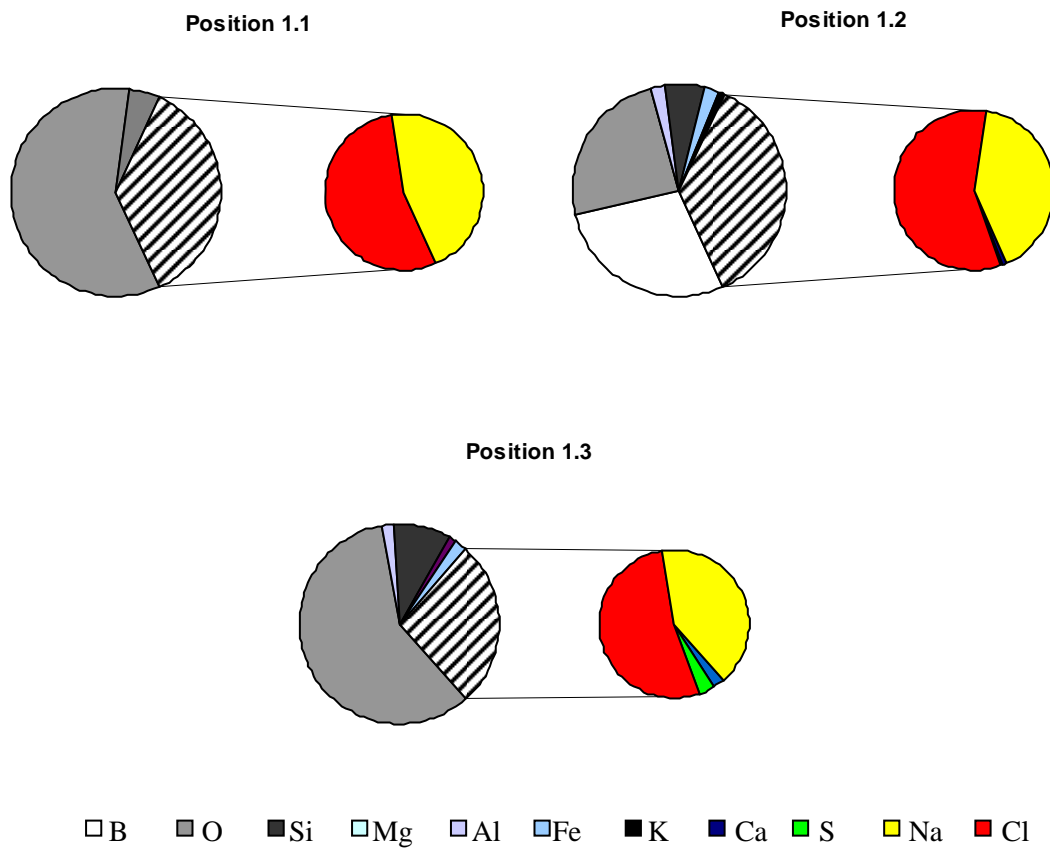
A sample (1) was taken from the deteriorated surface and analyzed by SEM-EDX in the three positions: 1.1 (250 μm \times 200 μm), 1.2 and 1.3, figure 4.

By evaluation of the found elements, their amount and distribution was it provided that: evenly distribution throughout the whole cross section indicated elements in matrix, whereas concentrations in isolated areas indicated polluting elements from a salt.

Overlapping mappings indicated elements from the same salt crystal.

Comparison of the element distribution in figure 4, shows that Na and Cl were the major pollutants in what concerns concentration. In position 1.1 Na and Cl were the only pollutants found. In position 1.2 high Na and Cl concentrations were found, but here Ca and S were also identified although at much lower concentrations. In position 1.3 a high, but relative lower sodium chloride content than in position 1.2 was found and also here a small content of calcium and sulfur was identified. Low calcium contents can originate from the lime mortar. Low sulfur contents can originate from the brick material itself. In bricks produced for restoration purpose low sulfate contents in especially bright bricks have been measured [Rörig-Dalgaard & Ottosen, 2008].

Presences of sulfate can according to Larbi (2004) originate from brick masonry or be caused by atmospheric pollution [Charola et al., 2007].



| Position | B | O | Si | Mg | Al | Fe | K | Ca | S | Na | Cl |
|----------|------|------|-----|-----|-----|-----|-----|------------|------------|-------------|-------------|
| 1.1 | - | 58.6 | 4.7 | - | - | - | - | - | - | 16.9 | 19.8 |
| 1.2 | 28.1 | 24.1 | 6.1 | 0.2 | 2.1 | 2.1 | 0.8 | 0.3 | 0.1 | 14.9 | 21.2 |
| 1.3 | - | 58.5 | 9.0 | - | 2.1 | 2.1 | 1.0 | 0.7 | 0.8 | 11.1 | 14.4 |

Figure 4. (Left pie charts) Element distribution between matrix (gray, black and blue colours) and presumed elements in salt crystals (hatched area). (Right pie charts) The enlarged area shows the proportionally distribution of the presumed elements in the salt crystals (intensive red, yellow, green and blue) The Boron measured in position 1.2 is unlikely and must be another unidentified element. (*Italic: matrix, Bold: polluting salt*)

Some of the mappings (by SEM-EDX) from position 1.1, 1.2 and 1.3 are shown in figure 5 and 6. In position 1.1 and 1.2 only Na and Cl were found in isolated areas.

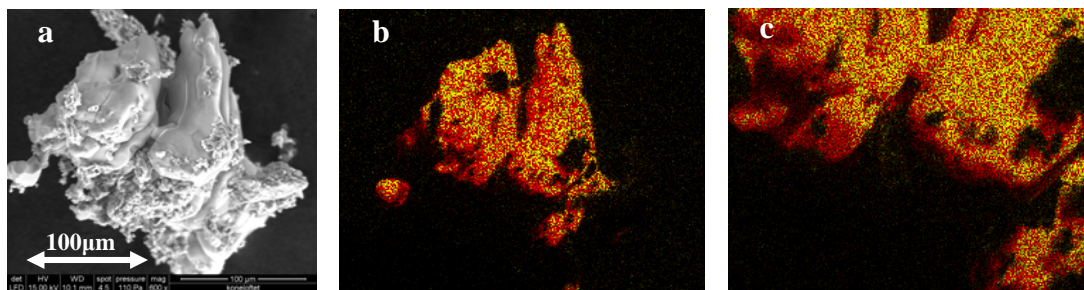


Figure 5. (a) ESEM picture of position 1.1. EDX mapping, chloride (red) and sodium (yellow): (b) in position 1.1. (c) in position 1.2.

Overlapping areas of sodium and chloride were seen in position 1.1 and 1.2 which indicates presence of NaCl. The sodium chloride crystal in position 1.1 is almost clean.

In position 1.3 Na, Cl, Ca, S and O were found in overlapping areas.

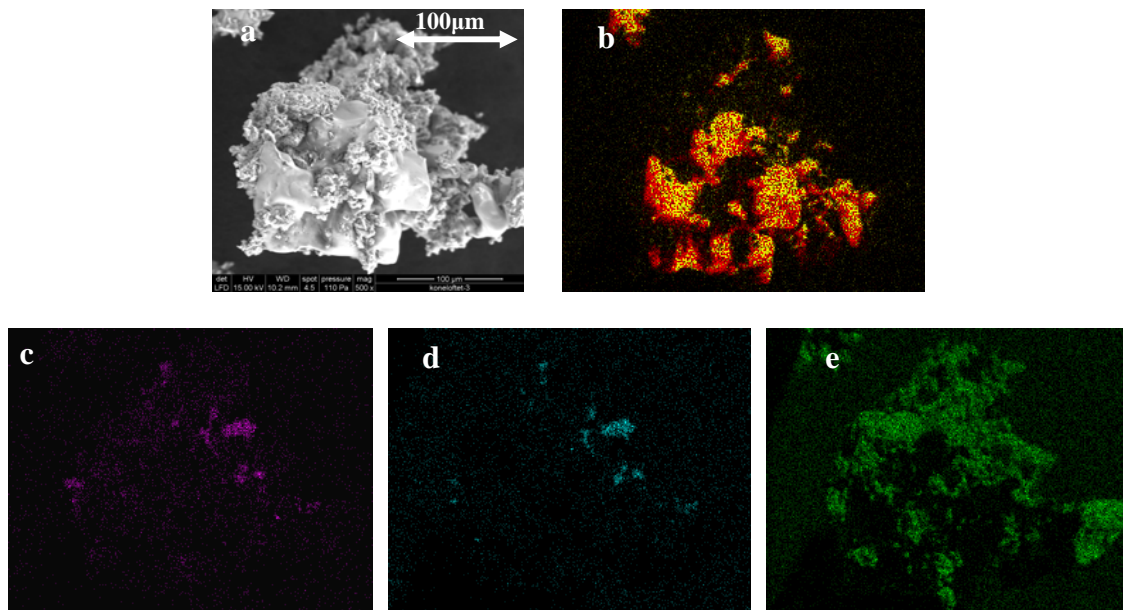


Figure 6. (a) SEM picture in position 1.3, SEM-EDX mappings: (b) chloride (red) and sodium (yellow) (c) calcium (d) sulfur (e) oxide.

Corresponding to mappings from position 1.1 and 1.2, overlapping of sodium and chloride in the main part of the cross section occurs and presence of sodium chloride crystals is therefore most likely.

Additionally, overlapping of calcium and sulfur are easily recognized and comparison with the oxide mapping also shows O in these positions and for this reason CaSO_4 is likely.

There was a general tendency for presence of sodium chloride in almost clean crystals.

5.2 Efflorescence at the upper side of the vault

A cement plaster covered the brick masonry vault at the upper side. In some areas efflorescence was visible. Plaster peeling was seen at few of the bricks but else no further damage was observed. A sample from the efflorescence was taken for identification of these salt crystals.



Figure 7. Visible efflorescence at the upper side of the vault.

Table 1. Element distribution in position 2.1, 2.2, 2.3 and 2.4. Distributed of matrix and polluting salt.

| Position | O | Si | Mg | Al | Fe | K | Ca | S | Na | Cl |
|----------|------|-----|-----|-----|-----|-----|------|-----|------|------|
| 2.1 | 21.7 | 1.1 | - | - | - | 1.1 | 3.1 | 0.5 | 10.8 | 61.8 |
| 2.2 | 55.5 | 5.2 | - | 2.2 | - | 3.7 | 16.8 | 3.0 | 6.0 | 7.7 |
| 2.3 | 47.9 | 4.9 | 0.5 | 1.9 | 171 | 3.1 | 17.3 | 0.8 | 10.5 | 11.4 |
| 2.4 | 66.3 | 3.1 | 0.5 | 1.0 | - | 5.1 | 12.8 | 1.4 | 3.6 | 6.3 |

Italic: matrix

Bold: polluting salt

In sample 2, Ca, S, Na and Cl were detected as in sample 1. Additional K was also found as polluting element. Potassium as pollution ion was also reported by [Larbi, 2004] as Potassium sulfate (K_2SO_4) in masonry mortars originating from the adjoining bricks.

Comparison of SEM-EDX mappings with the SEM pictures were carried out to identify the salt crystals and their shape, figure 8.

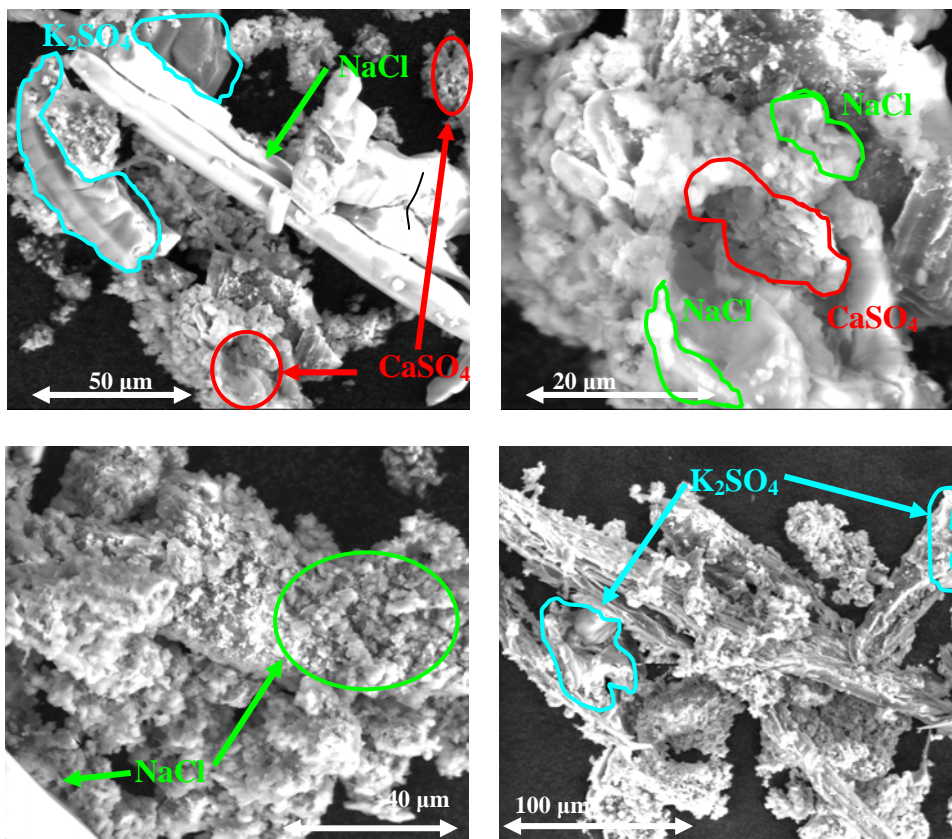


Figure 8. The salt crystal distribution and composition in four different positions. **Position 2.1 (upper left):** Long Sodium chloride crystal, smooth surfaces (dense crust) K_2SO_4 , bubbled (cuttum balls) $CaSO_4$ (S:0.5 wt%). **Position 2.2 (upper right):** Blurry salt crystals by presence of higher sulfate content (S: 3.0 wt%), outside the marked areas evenly K, Ca and S distribution was detected. **Position 2.3 (lower left):** NaCl bar at the lower left corner, evenly K, Ca and S distribution throughout the rest of the section. **Position 4 (lower right):** NaCl skeleton, two K_2SO_4 areas and the rest of the white areas where identified as $CaSO_4$.

At the conditions at the sampling in Vor Frue Monastery, NaCl tends to form relative long smooth, crystals in some cases serving as background skeleton for other salt crystals. K_2SO_4 tends to form smooth crystal with varying shapes (shorter/longer or wider/narrow) positioned on or in between other salt crystals. Contrary to NaCl and

K_2SO_4 , $CaSO_4$ seems to form bobbled or bloated crystals. Formation of these bobbled crystals seems to be a visualization of the traditionally described volume expansion by hydration by crystallization of salts and their re-crystallization from a lower to a higher hydrate. Presence of these bobbled or bloated crystals was especially pronounced in position 2.2 in where high sulfur content was detected. Based on the pictures from position 2.1-2.4, significant differences occurs between the formatted crystals and differences in deteriorating effect could be related to these variations in salt crystal formation.

5.3 Lime layer from the floor below the vault

A lime layer was found at the floor below the vault. Since deterioration had occurred the reason for this deterioration was aimed. In case of salt induced deterioration the deteriorating salt must be present in the fractures. According to [von Konow, 2002] salt crystallization can occur at the interface between the underlying brick material and the lime plaster and this was also expected in the present case. The thickness of the present lime layer was 0.4 mm which must be a consequence of the established evaporation zone at the actual climate conditions.

The repelled lime layer was investigated in ESEM (table 2) and analyzed by SEM-EDX (figure 9). The investigation was made on the fracture side of the sample since the deteriorating salt crystals were expected to be there. One side of the sample had a painted surface so the opposite side was presumed to be the fracture side.

Table 2. SEM-EDX results from position 3.1 and 3.2 in the repelled lime layer.

| Position | O | Si | Mg | Al | K | Ca | S | Na | Cl |
|------------|------|-----|-----|-----|------------|-------------|------------|------------|------------|
| 3.1 | 57.2 | 1.5 | 0.4 | 0.2 | 0.6 | 35.4 | 3.5 | 0.5 | 0.7 |
| 3.2 | 63.6 | 4.0 | 2.6 | 0.4 | 1.1 | 24.5 | 0.9 | 1.2 | 1.7 |

Italic: matrix

Bold: polluting salt

In both position 3.1 and 3.2 sodium and chloride is present, however only to a relative small content compared to the samples from position 1 and 2. Additionally, considerable amounts of K, Ca and S were present.

In figure 9, the top within the red ring is very characteristic and the elements: Ca-S-O was identified here which leads to this part most likely being gypsum ($CaSO_4 \cdot 2H_2O$). O and Ca were found almost throughout the whole cross section whereas S only was mapped along the fractures in general, figure 10. In position 3.1, the S content was relatively higher than in position 3.2 and covers a larger area, see figure 10.

Similar to position 3.2, S in position 3.1 is present from the fracture but here additional continuing over a larger area covering almost the whole shown area. Since gypsum was the only salt present at the fracture, it seems likely that repulsion of the lime plaster is caused by the gypsum formation.

Gypsum was also present at the fracture, in position 1.3 however only 0.8 wt% S was found and still extensive deterioration was visible (figure 6). However, it must be taken into account that the deterioration could have been ongoing over a long period: decades or even centuries and it seem like even small contents sulfur can be damaging. This is supported by [Scherer, 1999], which through calculations argues that salt crystal induced fractures can not be caused by crystallization in a single pore, contrary it requires crystal growth in a whole region of the material comparable in size to the flaws size.

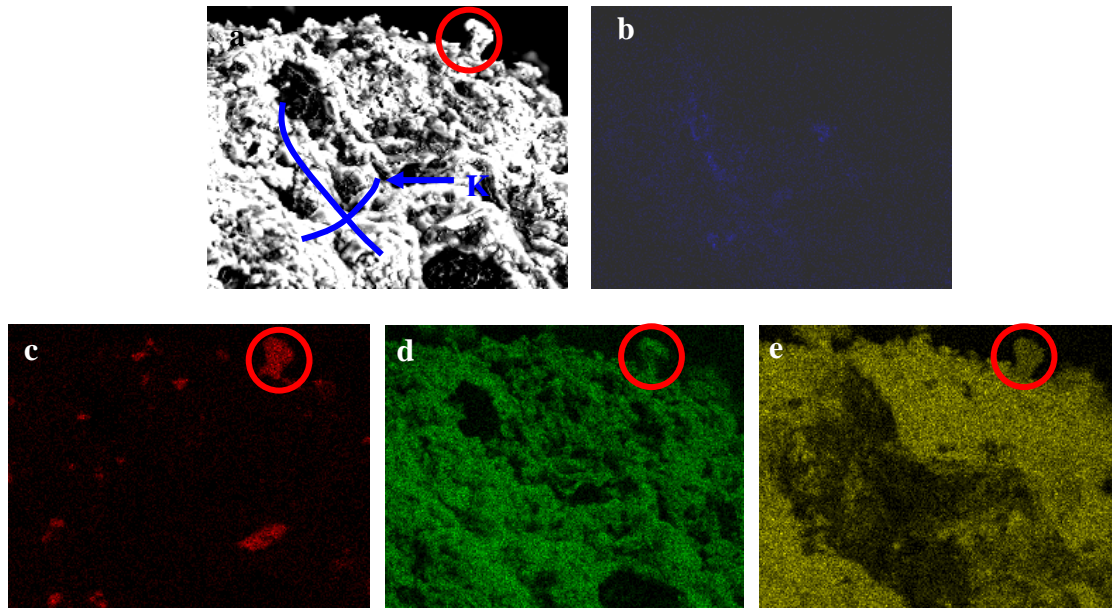


Figure 9. (a) The sample with potassium from position 3.2. Potassium is marked as the blue lines (b) potassium element distribution. Coincidence of sulfur (c), oxygen (d) and calcium (e) in some areas e.g. along the fracture and inside the red ring. The fracture is at the top of the picture.

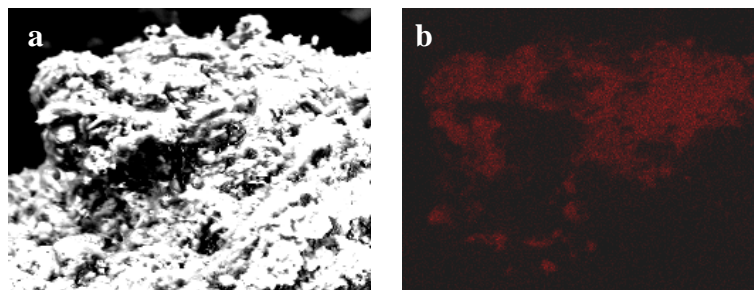


Figure 10. (a) Sample picture from position 3.1. The fracture is at the top of the picture (b) sulfur distribution.

5.4 Lime piece from the floor below the vault

Also a few millimetres thick lime layer (3.6 mm) was found in position 4 at the floor in the birds room and analyzed. Again, since deterioration had occurred a possible explanation for this was searched for at the fracture.

Table 3. SEM-EDX results from position 4.1 (the repelled lime piece from the floor).

| Position | O | Si | Mg | Al | K | Ca | S | Na | Cl |
|----------|------|-----|-----|-----|-----|-------------|------------|------------|------------|
| 4.1 | 65.8 | 1.9 | 0.3 | 0.5 | 0.4 | 28.7 | 0.6 | 0.9 | 0.9 |

Italic: matrix

Bold: polluting salt

Again a low sulfur content was measured in position 4.1 compared to position 3.1.

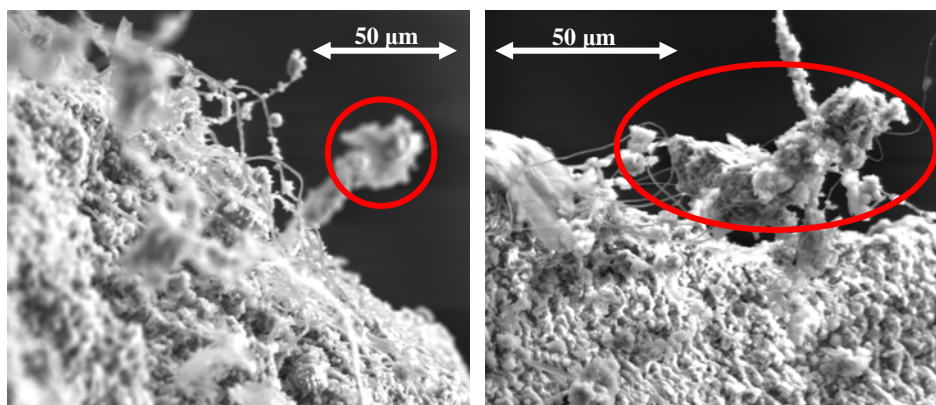


Figure 11. Position 4.1 (left) Inside the red ring a bar with a ball in the end as seen in figure 9 due to gypsum formation. Position 4.2 (right) An area is just about to be pushed of (cross section not analysed in EDX).

Compared with deterioration of the thin lime layer (sample 3), the mechanism seems to be the same, only the repealed layer was here 3.6 mm thick instead of 0.4 mm thick. This may show a deeper laying evaporation zone where the lime layer peeled off in position 4 than 3. This suggests that even thicker layers (few millimetre thick lime layers) can be pushed of with the present salt contents, mainly due to the gypsum content. Lewin (1982) also reported surface decay thicker than a paint layer, in the order of a millimetre.

5.5 Lime piece from a windowsill in the Birds' room

A repealed lime layer was also found in the windowsill, meaning deterioration had occurred and the fracture was studied. Since the piece was found in the windowsill it is considered unlikely that it originates from the vault. However, the lime piece was investigated too in case of similarities with the other samples.

Table 4. EDX results form position 5.1, 5.2 and 5.3 in the lime piece from the windowsill.

| Position | O | Si | Mg | Al | Fe | K | Ca | S | Na | Cl |
|----------|------|------|-----|-----|-----|-----|-----|---|------------|------------|
| 5.1 | 77.2 | 14.2 | - | 4.6 | - | 3.9 | - | - | - | - |
| 5.2 | 69.6 | 15.9 | 0.6 | 5.6 | 3.5 | 2.1 | - | - | 1.8 | 0.9 |
| 5.3 | 48.6 | 29.3 | 1.1 | 8.3 | 6.1 | 3.9 | 1.0 | - | 1.2 | 0.6 |

Italic: matrix

Bold: polluting salt.

In position 5.1 no polluting salts were found, in position 5.2 and 5.3 few sodium chloride areas were found. In general limited Na and Cl areas and absence of S was seen at the EDX mappings.

The SEM pictures from both the fracture and from the middle part (figure 12) has a significantly different look than all the other samples and neither salts were found by the EDX mappings nor seen at the SEM pictures. Additionally, this was the only sample without sulfur.

This suggests that the material found in the windowsill had another deterioration mechanism than for sample 1 - 4. These results suggest that the piece had neither direct contact to nor similarities with the deterioration in the vault and that the deterioration may have other reasons e.g. thermal expansion, hygroscopic shrinkage [Larsen & Nielsen, 1990] or frost damage since lower temperatures can occur by the window compared to in the middle of the room.

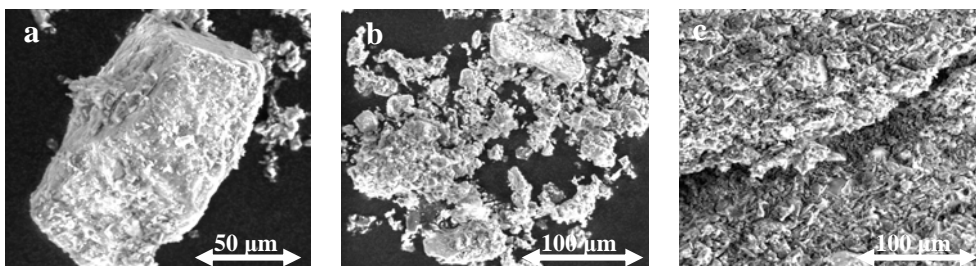


Figure 12. Three SEM pictures from the found lime piece in the windowsill. (a) Position 5.1 (b) Position 5.2 and (c) Position 5.3.

6. Discussion

The SEM-EDX analysis showed presence of Na, Cl, K, S and Ca in the extracted samples.

It was provided that overlapping element mappings in the same isolated areas indicated the polluting salt. Examination of sample one from the masonry at the loft showed presence of almost clean NaCl crystals. Presence of NaCl in the masonry of other ancient buildings was thought originating from storage of perishable food or sea spray [Larsen, 1999] and NaCl pollution have been measured in several Danish churches: Brarup church [Larsen, 2007], Fanefjord church [Larsen, 2000] and Kirkerup church [2000b]. It is therefore likely that the present NaCl contamination originates from storage of perishable food as well. This could explain why the deterioration of the masonry is only pronounced in the south-west to north-west corner whereas the rest of the masonry seems unaffected.

The efflorescence at the upper side of the vault were found to contain the elements Na, Cl, K, Ca and S. The overlapping EDX mappings likely the presence of the salts NaCl, K_2SO_4 and $CaSO_4 \cdot 2H_2O$. By examination of a damaged church vault in Brarup Church, Denmark, 1.6 wt% sodium chloride was measured in the vault and resulted in powdering of the bricks. In the powder above the vault the same amount of sodium chloride was measured as in the bricks but in the powder there was in addition a high sulfate content. Larsen (2007) suggests, that the presence of sulfate, sodium and chloride in combination with the existing calcium from the mortar or lime layer results in gypsum ($CaSO_4 \cdot 2H_2O$) formation and in combination with varying climate gypsum formation is the reason for the deterioration.

Common for the repealed thin lime layer (0.4 mm) and the thicker lime piece (3.6 mm) was the presence of overlapping Ca, S and O mappings along the fractures whereas the present Na, Cl and K was mapped inside the cross section. This indicates that gypsum is formatted along the fractures and results in the repulsion of the lime layers. The presence of e.g. NaCl lower the deliquesce humidity of gypsum as described in section 2 and thereby accelerated the gypsum induced deterioration. Charola & Koestler (1986) also showed presence of gypsum in the fractures on limestone from four monumental buildings in Vienna by SEM studies and attributed the deterioration to the presence of gypsum.

In the Regalia Room in the Archbishop's Palace in Trondheim, sodium chloride, sodium nitrate and sodium sulfate were considered responsible for the deterioration [Franz & Storemyr, 2000]. Also Zehnder (2007) attributes gypsum a determining factor for the deterioration of wall paintings in three churches in Switzerland.

In summary gypsum has been identified in several places where severe deterioration has occurred and the deterioration pattern in the Carmelite Monastery in Helsingør, Denmark is therefore in good consistence with previous observations here shown with SEM-EDX analysis.

7. Conclusion

At the loft, above the vault unusual high sodium and chloride contents were found and storage of perishable food in ancient time is the most likely reason for this. At the upper side of the cement plaster covered vault efflorescence of sodium chloride, potassium sulfate and calcium sulfate were found and only minor deteriorations. However, this could be due to the presence of the cement plaster. Below the vault extensive deterioration of the valuable paintings had occurred. At the floor below the vault both a thin lime layer and a thicker lime piece was found and common for these were presence of S along the fracture at all the measured positions whereas the sodium chloride content was relative low in these positions and located in the middle of the cross section.

On basis of element content and distribution found by SEM-EDX, K, S, Ca, Na, Cl were found as polluting elements. K, Na and Cl were found in areas within the cross sections and contrary S and Ca were identified at the fractions. It is suggested that the presence of sodium chloride for several centuries combined with sulfate from the bricks, carbonate from the lime mortar, accelerated gypsum formation through repeating dissolution-crystallization cycles had resulted in the extensive deterioration of the birds' room at Vor Frue Monastery in Denmark.

The fractures did most likely come into existence as a consequence of the salt formation and material layers are pushed of. The shape of the formatted gypsum at the fractures is a bar with a ball in the end.

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Discussion of perspectives and future work

During the work with the papers I-VI, additional correlations and new questions appeared. They are described in the following related to: 1. Changing experimental parameters, 2. Electroosmotic dewatering followed through the resistance, 3. Electrokinetic induced matrix changes and 4. Future work in relation to desalination of a salt contaminated vault. These coherences were found in relation to the work with papers I-VI and the following can not be read independently of the papers.

1. The influence of changing experimental parameters during electrokinetic treatment

The aim with optimization experiments in the present work regarding current strength and water content was made in order to obtain the clearest possible results of other primary parameters during the laboratory experiments e.g. the effect of new developments to improve efficiency and possible desalination velocity.

Nystrøm (2004) conducted optimization experiments on electrokinetic remediation of heavy metals in harbour sediments and Pedersen (2002) on electrokinetic fly ash remediation to increase the removal efficiency of heavy metals.

The optimization in the present work of the current strength was made on basis of their work, varying the current strength above and below what they found appropriate and by following the total resistance of the system.

Several authors have described electrokinetics to be dependent of the water content [Friese & Protz, 2002], [Buchwald & Goretzki 1996], and that water saturation is necessary to make the method working [BPS, 1991]. In contrast to this, [Friese & Protz, 2002] carried out electrokinetic desalination of masonry and murals with a water content of 3-4 wt%.

1.1 Current optimization

For electrokinetic remediation of fly ash in laboratory scale the optimal current strength was between 40 mA and 80 mA [Pedersen, 2002]. At 80 mA the need of care was high as pH adjustments had to be made several times a day to ensure an optimal current utilization. This was found inappropriate due to the normal working hours.

For electrokinetic remediation on harbour sediments in laboratory scale Nystrøm (2004) found that use of 90 mA resulted in formation of too much foam and the experiment had

to be stopped occasionally. Contrary by use of 70 mA the experiments were running without any problems.

In the present study the current strength was varied between 20 mA, 40 mA and 80 mA. The hypothesis was that increasing current strength would increase the resistance across the setup, this again would result in increased heat and thereby increase the evaporations influence on the total system. This again would result in less possible ion extraction (possibility for less accumulated ions in the clay as the salts probably are transported towards all the brick surfaces through evaporation).

The results for the three experimental rows (20 mA in 4 weeks, 40 mA in 2 weeks and 80 mA in one week) were compared related to the consumed current. In this way the influence of the current strength versus evaporation was investigated, figure 1.

It was seen, that significant different water contents existed after ended experiments dependent of the experimental duration. It was seen that the evaporation increased significant with increasing duration time indicating the covering by the plastic wrapping was not optimal for a several weeks experiment. During the evaporation of water ions must simultaneously have been transported towards the surfaces. This was tested by measuring the remaining chloride concentration in the bricks, figure 2.

By comparison of the remaining chloride concentration after a current consumption of 48384 C, corresponding to 1 week with 80 mA, 2 weeks with 40 mA and 4 weeks by application of 20 mA, some tendencies were seen. A lower chloride concentration was measured by application of 80 mA than by 40 mA after a current consumption of 48384 C. This indicates at least a similarly high effect by electromigration with an applied current of 80 mA and minor evaporation within 1 week than by application of 40 mA current in 2 weeks and the thereby increased convection during evaporation. However, the lowest chloride concentration was measured in the brick with an applied current of 20 mA during 4 weeks indicating that evaporation towards the surfaces has a significant effect. To prove these tendencies extracted chloride in the poultice should be measured. These experiments indicate that the clearest experimental results with the lowest evaporation are obtained by application of 80 mA.

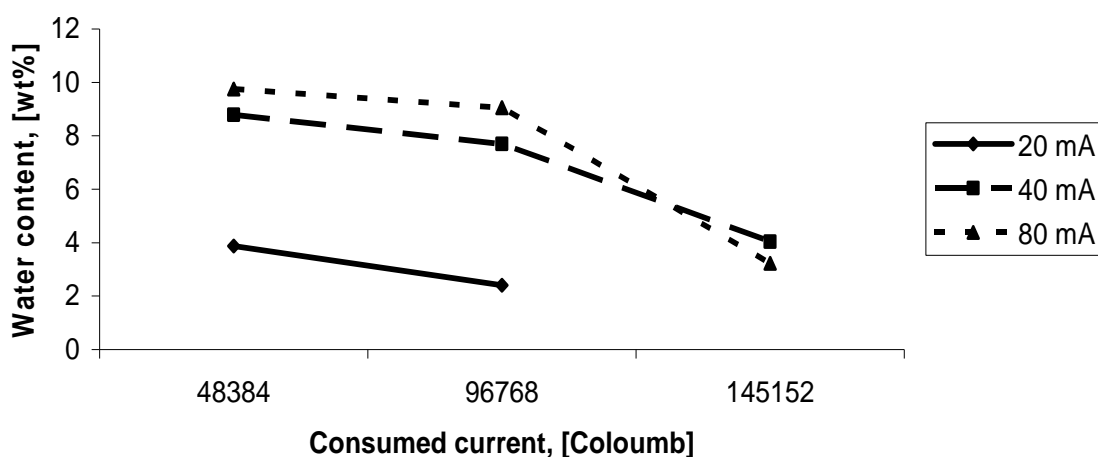


Figure 1. The influence of the duration time on the water content after the same consumed current, at the end of the experiment. The initial water content was approximately 13 wt%

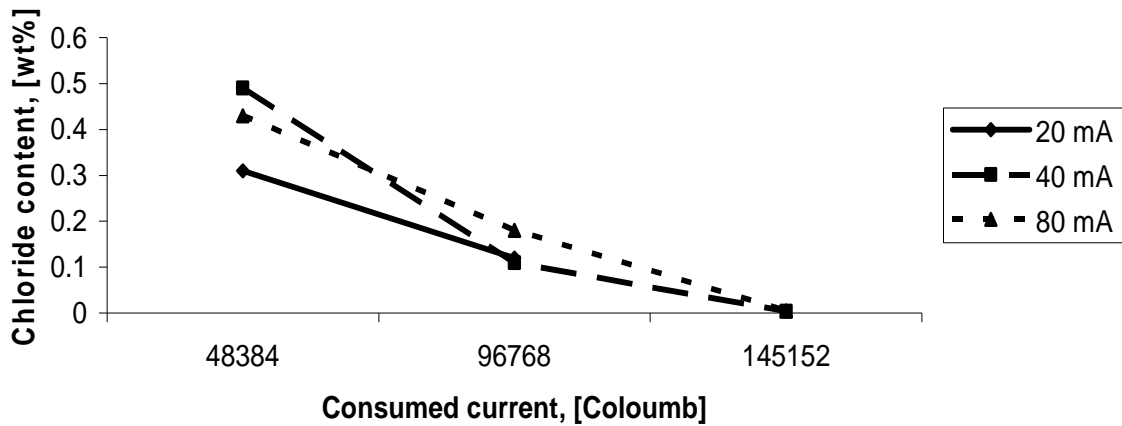


Figure 2. Remaining chloride content in the brick, as a function of current consumption. The initial chloride content was 1.0 wt%.

1.2 Varying water contents

Microbial growth on painted church vaults occurs in a humid climate and causes [Petersen, 1994]:

- Discoloring of surfaces in spots or bigger areas.
- Surface peeling caused by shrinkage or swelling.
- Failing attachment of painted layer due to decomposition of organic binders.
- Destruction of minerals (primary lime) caused by organic acids produced under the growth.
- Color changes caused by transformation of color pigment by oxidation or reduction processes.

Therefore the lowest possible water content is preferable during electrokinetic treatment. According to Buchwald & Goretzki (1996) the determining factor for ion transport is the pore filling degree (D):

$$D = \frac{w_{actual}}{w_{maximum}}$$

Where w_{actual} is the actual water content and $w_{maximum}$ the highest possible water content in the pores.

The pore filling degree is an indicator for the electrical resistance and thereby also a measure for ion transport efficiency. Buchwald & Goretzki (1996) describes a water pore filling degree of 50 % as necessary for ion transport in bricks.

The pore filling degree must be expected to give an indication of the total electrical resistance across a material independent of the actual material. However, material specific conditions e.g. pore size distribution must have an influence on the total electrical conductivity as well.

According to Friese & Protz (2002) presence of hygroscopic water can result in water contents up to 10 wt% by presence of salts. By presence of 1-2 wt% chloride the

corresponding water content is around 3 wt% which was sufficient to establish the needed electric field, though every 14th. day water had to be supplied to ensure the necessary water content of 3-4 wt% [Friese & Protz, 2002].

Since the total resistance in a moist material increases continuously with decreasing moisture contents there will be no precise limit below which electrokinetic effects ends. The electrokinetic effect decreases continuously with the increasing total resistance across the material.

2. Electroosmotic dewatering followed through the resistance

Coherence between the change in the total electric resistance and the remaining water content was found which made it possible to follow the dewatering process non-destructive.

In Rørig-Dalgaard (2002) the total resistance in a brick was found by capillary suction to a wanted water content with distilled water and subsequently measure the resistance. See figure 3.

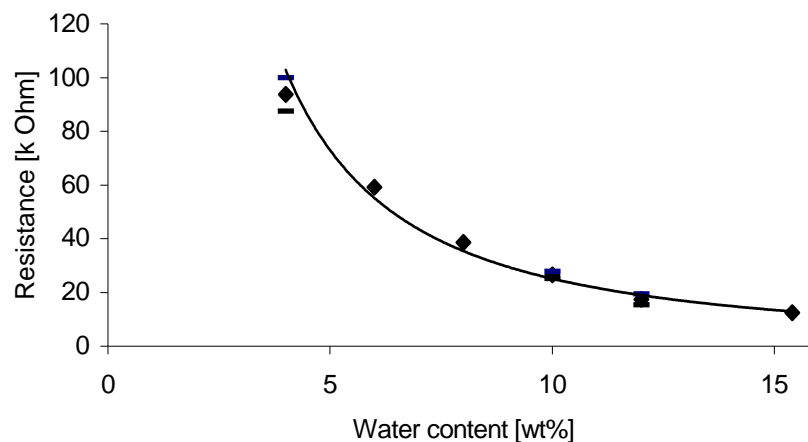


Figure 3. Measured total resistance across the brick type “Wewers red” at varying tap water contents, [Rørig-Dalgaard, 2002].

In the present study “Falkenløve red” bricks were used for desalination experiments and all experiments were carried out with capillary saturated bricks with 1.0 wt% chloride (added as NaCl). The experiments were ended after varying duration. The final voltage of each experiment was related to the average water content from 9 drilling samples from the whole brick. The coherence is shown in figure 4 both related to the measured voltage and the total resistance across the brick. The resistance across the brick was measured just before the experiment was ended and the water content was subsequently determined by mass loss after drying at 105°C.

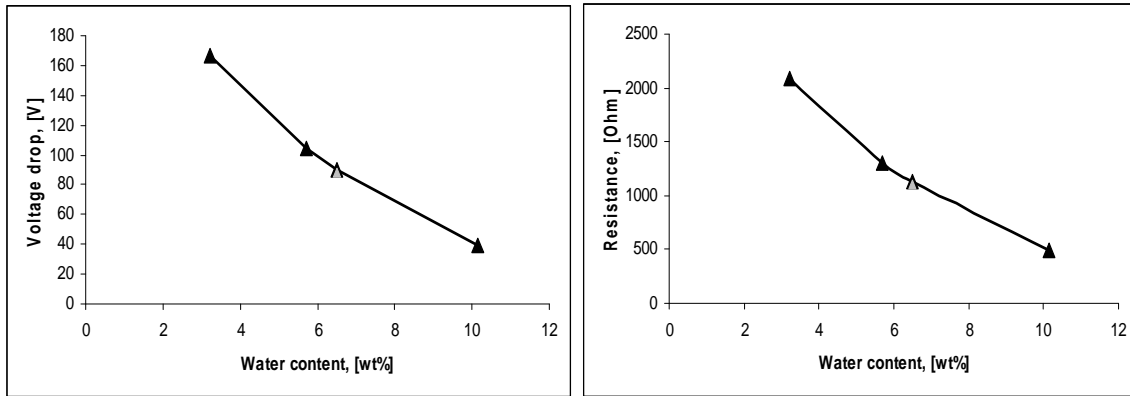


Figure 4. The coherence between final water content and voltage/resistance in Falkenløve. The gray marks are from additional measurements showing good repeatability of the results.

The measurements indicate an almost exponential decreasing tendency between the total resistances across the brick at increasing water contents. A smaller resistance increase occurs by reduction of the water content from relative high water contents e.g. from 10 wt% to 8 wt%, than from 6 wt% to 4 wt% which results in a duplication of the resistance.

Comparing the resistance measured throughout the present experiment with the brick type “Falkenløve red” with the measured resistance in the brick type “Wewers red” the relative change as a function of water content seems similar. This indicates that the water content is the most important factor related to the total resistance changes in an applied electric field provided the ion content is below “the point of starting dewatering” [Rörig-Dalgaard & Ottosen, 2008 E]. This also indicates that the variation in clay brick material is less determining than the water content. These coherences were used for assessment of actual water contents in other experiments and showed good reproducible results.

3. Electrokinetic caused matrix changes

The extent of the changes induced by the electrode reaction (discoloring, pH changes, weathering of the material) in bricks was investigated after the development of the poultice described in Rörig-Dalgaard & Ottosen (2008).

3.1 Avoiding discoloring

Most desalination experiments were carried out with stainless steel (any of various steels alloyed with at least 10 percent chromium) electrodes since they are cheaper and the desalination/dewatering effect itself is only minor affected by the electrode material. However, decomposition of the anode began rapidly and resulted in extensive iron contamination of the poultice and in areas of the bricks adjacent to the anode poultice. An electrode mesh of oxide coated titanium donated by P C International was tested to avoid discoloring of the brick



Figure 5. Brick after use of an oxide coated titanium anode. No visible discoloring from the anode. The white areas are kaolin clay and can be minimized by use of e.g. porous paper between the brick and the kaolin clay.

Use of the oxide coated titanium anode, showed as expected no discoloring of the brick, but resulted in an obnoxious smells from chloride gas during the test by application of 40 mA, whereas by use of stainless steel anodes no chloride smell was noticed. This was supposed to be due to chloride gas formation by use of inert electrodes and presence of chloride ions in the vicinity of the anode (see chapter 3). This suggests that a lower current strength would be preferred by use of this electrode.

3.2 Use of a porous paper for avoiding clay residues

Discoloring from the electrodes was avoided by use of an inert anode, though a thin layer of clay remained after removal of the poultice. In some cases: (i) this layer is regarded inconsiderable and acceptable, whereas in other cases (ii) when e.g. placed directly on a valuable paint would be unacceptable. In case of (ii), use of a porous paper could be tested to avoid any trace of clay residues. To obtain a good conductivity through the paper, this can be wetted in distilled water before use. This remains to be tried.

3.3 Measured pH after ended electrokinetic treatment – Related to different brick firing temperatures

Electrode reaction induced pH changes of the original material was measured after desalination of bright, medium and dark colored bricks. The initial chloride content of 1.0 wt% (added as NaCl) was reduced to below 0.01 wt%. The pH measurements were related to the distance to the electrodes since the most significant pH changes were supposed to occur closest to the electrodes.

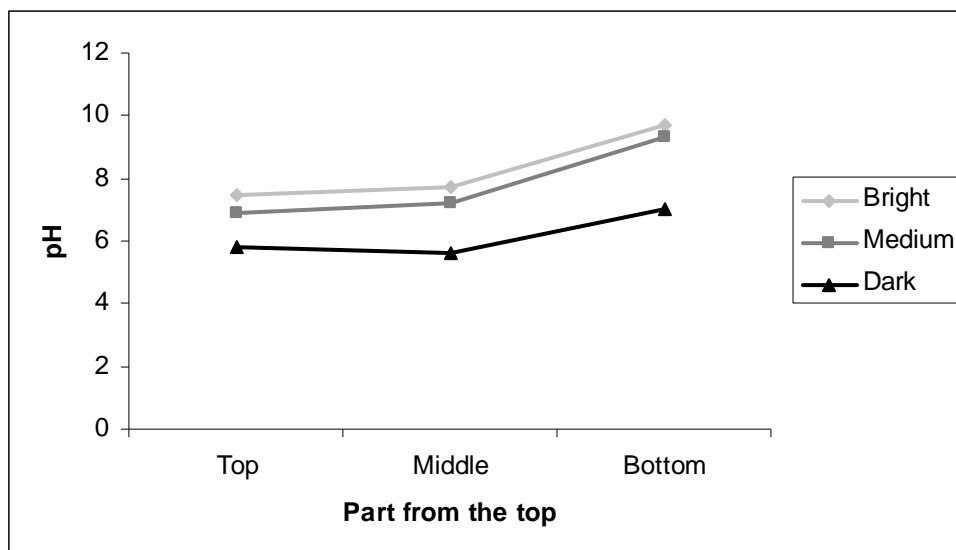


Figure 6. pH in the bricks after ended desalination treatment as a function of color (Bright, Medium and Dark) and distance to the electrodes (Top, Middle, Bottom). The initial pH was 8.5 ± 0.4 .

Figure 6 shows a tendency for highest pH in the bright colored brick, lower for the medium colored brick and lowest for the dark colored brick. The initial pH was similar for the three types; 8.5 ± 0.4 . After ended desalination the average pH in the bricks was 8.3; 7.8 and 6.1 for the bright, medium and dark colored brick respectively. Additionally, the brick materials are most affected in the upper 2/3 of the brick (corresponding to the upper 10 cm) whereas the lowest 1/3 of the brick (Bottom part) is less affected of the pH changes.

The bright colored brick is least affected by the pH changes. This may be because the bright colored brick which is fired at the lowest temperature had the highest initial CO_3^{2-} content as could be expected due to the least decomposition of $\text{CO}_3(\text{s})$ to $\text{CO}_2(\text{g})$ and thereby also the highest acid buffering capacity against acidification. CaCO_3 is present in an original clay mixture for brick production [Rasmussen, 1992] and starts to get decomposed at temperatures above $830\text{-}900^\circ\text{C}$ [Cultrone et al., 2001].

The missing difference in carbonate concentrations as a function of brick firing temperature in Rörig-Dalgaard & Ottosen (2008 B) could be due to the used methods not being sensitive enough at very low concentrations. The medium colored brick seems to have a medium buffering capacity against acidification and the dark colored seemed to possess the least acid buffering capacity.

These measurements indicate that Falkenløwe red brick has a pH buffer capacity in contrast to the tests in [Rörig-Dalgaard & Ottosen, 2008 B]. This suggest that the chosen test for buffer capacity gives a misleading result and a lower liquid to solid ratio between dry power (5 g dry powder to 25 g liquid) or lower acid/base concentrations might be appropriate and give a more reliable result related to the bricks acid and maybe also base buffer capacity.

These measurements indicates that carbonate in the brick matrix to some content is dissolved during the electrokinetic treatment. To avoid this decomposition of carbonate pH must be kept above 6.

3.4 Matrix changes. Observations in SEM

The optical difference between treated and untreated bricks was investigated by SEM, of the brick type “Falkenløwe red”, see figure 7. The pH of the bricks had changed during electrokinetic treatment in the treated bricks for this SEM analysis.

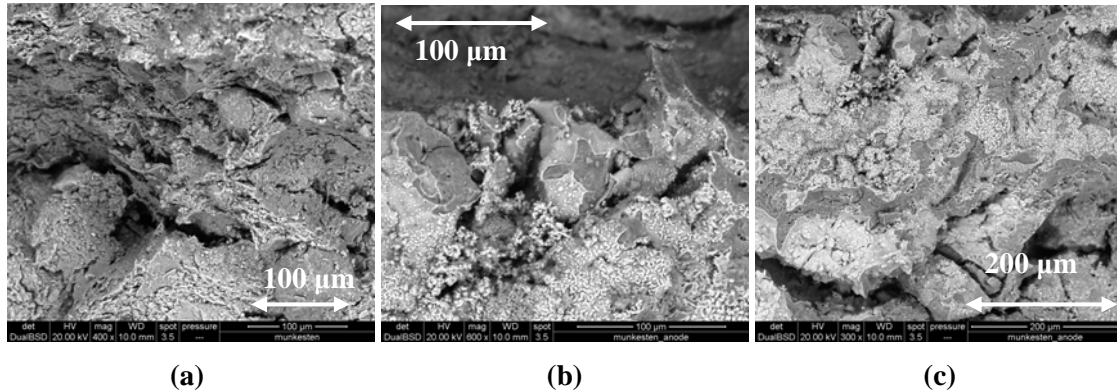


Figure 7. (a) Non electrochemical treated brick (salt contaminated bricks of the type Falkenløwe red). (b) Electrokinetic treated brick regarded at the border between brick and kaolin clay (c) Electrokinetic treated brick regarded in inner areas.

Comparison of the treated and acidified brick to the untreated brick showed that the internal surfaces in the treated brick had changed look from a landscape with sharp hills to rounded surfaces similar to stones that have been placed in the sea for some time and rounded by the water. This change in shape of internal surfaces might be similar to weathering induced changes.

After crumbling of the mortar as observed during the work described in Rørig-Dalgaard et al. (2008 D), and the present visual changes of the brick, additional improvements of the cathode poultice was carried out to hinder acidification of the bricks. The cathode poultice improvements are described in [Appendix 1]. Matrix related changes after improvement of the cathode poultice (hindering diffusion of the acetic acid into the brick) has not been investigated yet, but will naturally be done in the future. However, the new cathode unit has a pH of 7.6 in the contact area and it is therefore considered as a significant improvement in order to minimize the matrix changes during future treatments.

4. Present knowledge level

In the present work documentation was carried out in steps to minimize misinterpretations and since only little documentation was available before the study was started, focus was on the simplest setup: desalination of single bricks. A desalination effect was also measured on a more complex system: a dry brick masonry wall section with murals, however this treatment was not optimized during the present study due to a short of time.

For completely documentation of the electrokinetic desalination of painted church vaults many essential questions remain unanswered e.g.: how proceeds electrokinetic desalination in a combined brick and mortar system? What is the effect of the intervening lime mortar? Will the mortar hinder desalination? Will accumulation of ions occur in the mortar? Is it possible to obtain the same high desalination efficiency on

existing structures with limited moisture supply as has been obtained on capillary saturated bricks? Is it possible to increase the desalination efficiency by use of a microclimate to ease dissolution of the precipitated ions? Can pigment changes be observed as a consequence of the applied electric field in a microscope or by other methods used by conservators? Can the electrode units only be placed on the opposite side of the vault as the murals?

Even though many essential questions has to be answered before the method can be applied on salt contaminated brick masonry church vaults with murals, the fundamental effect and the possibilities of an applied electric DC field has been documented in the present work. All developments in the present work (mainly on single brick setups) were made with the aim to be applicable on traditional church vaults, however, whether the developments are applicable on traditional church vaults has to be investigated in future work.

5. Future work in relation to desalination of a salt contaminated vault

In the autumn of 2008, this PhD study continues in a Post-doc study with focus on electrokinetic desalination of an existing salt contaminated vault. The new study is financed by the Augustinus Foundation. The aim is to optimize the electrokinetic method in pilot scale in order to obtain the same good results in pilot scale as in the laboratory experiments.

Some special conditions in existing churches are expected to have an influence on the desalination process and must be considered.

5.1 Natural variation in the relative humidity and its effect on dissolution of salts

The climatic influence on salt distribution within structures is significant. This has to be taken into account, especially when working in unheated rooms where the seasonal changes have a determining impact on the indoor climate. Especially the relative humidity changes are of major importance when dealing with salt induced deterioration. Since the salts are causing problems due to dissolution-precipitation cycles it must be assumed they are at least partly dissolved in some periods.

It should be considered whether advantage can be taken of the seasonal changes so the treatment is performed when most salts are in dissolved form. Electromigration is a rather fast transport mechanism and can presumably be carried out within few months in the relative thin vaults (approximately 14 cm thick as in the all tests in the present work) during periods with high relative humidity's if the salts are dissolved.

The dissolved salts (ions) should preferably be transported towards the top of the vault where the salt accumulating poultice is thought to be placed. The transport towards the top of the vault is preferred to avoid any action on the sometimes very fragile murals surfaces.

The natural liquid transport with ions induced by changes in the climate, occurs as a part of a drying out process. A high relative humidity below the vault is needed to ensure

that the salts are dissolved and can be transported. Therefore the summer with high relative humidity seem to be the best time of the year for desalination since the indoor climate traditionally has a high relative humidity whereas the climate on the top of the vault has a lower relative humidity [Larsen, 1999]. There is a lower relative humidity on top of the vault because of higher temperatures, caused by heating from the sun on the roof and due to ventilation below the roof. If the actual relative humidity is too low for an electrokinetic treatment construction of climate chamber below the vault as in Larsen (1999) could be the solution.

Whether the natural variation in the relative humidity is sufficient to dissolve the present ions sufficiently and whether the actual present water content is sufficient to establish desalination by electromigration could be investigated in laboratory tests. Bricks with nucleated salts of relevance can be placed in a climate chamber with a relative humidity above the deliquesce point and subsequently measure the effect on an applied electric DC field.

5.2 Additional moistening

Provided the climate changes during the year and use of climate chambers are not sufficient to establish a working desalination additional moistening must be considered. During pilot plant experiment with the wall section in paper (V) in a dry laboratory climate, the limiting factor seemed to be the moistening of the brick masonry to dissolve the precipitated salts and ensure enough water for the electromigration. In connection with the compress plaster method similar problems have been studied. Recent knowledge within this field will be gathered at the International Conference “Salt Weathering on Buildings and Stone Sculptures” in Copenhagen 22. - 24. October and on the final workshop for the EU project “Assessment of desalination mortars and poultices for historic masonry (2006-2009)” in Köln winter or spring 2009 (not finally decided yet).

5.3 Salt mixtures

Also the actual present ions in the vault to be desalinated are of importance for the desalination process and will be studied in laboratory tests during the Post doc study. The dissolution of precipitated salts is dependent on the present salts deliquesce point and the presence of possible double salts [chapter 2]. Additionally, each ion is transported with varying velocity [chapter 3] and the type of present ions will for this reason have an effect on the desalination velocity [chapter 3].

The most traditional ions in vault construction are: Sodium (Na^+), Potassium (K^+), Chlorine (Cl^-) and Nitrate (NO_3^-). However, calcium, magnesium and sulfate have also been measured in some samples but at low concentration [Larsen, 1999], however, they might have an influence on the desalination process anyway and should therefore be taken into account, too.

Empirical investigations in relation to wall paintings, supported by statistical analysis showed that the salt distribution not only varies with location but also in dept and over time. It is suggested to perform sampling during periods of low relative humidity [Sawdy & Price, 2005] and this has to be taken into account, too.

5.4 The influence of the temperature on the desalination effect

Also low temperature during the winter is rather special in relation to church vaults. There are low temperatures due to the missing isolation of the roof. Though, low temperature are not expected to hinder the desalination effect as preliminary experiments at temperatures down to -10°C to -15°C did not have a negative effect on the desalination effect [Ottosen et al., 2006]. However, the desalination velocity is expected to decrease by decreasing temperatures as e.g. found for electro-dialytic remediation of cobber, zinc and lead contaminated kaolin clay in [Kristensen, 1998]

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Overall conclusion

During the present study the electrokinetic effect for desalination was carried out in steps towards possible application on salt contaminated church vaults with murals. However, the focus was on the simplest setup: desalination of single bricks. Desalination and dewatering of capillary saturated single bricks was documented, including identification of side effects and optimization of the process. A desalination effect was also shown in a more complex setup: a dry brick masonry wall section with murals. However, this very first non optimized electrokinetic treatment of the dry wall section must be improved before the same high desalination efficiency can be obtained as measured during the desalination of the capillary saturated single bricks.

A major part of the work was related to the necessity to improve and optimize the electrokinetic process. New electrode units were developed to prevent the acid and base produced during the treatment to enter the brick masonry and to optimize the desalination effect. The new developments were the calculation of actual needed neutralization effect (dependent of current strength and duration) and addition of needed buffer component. These new developments were the basis for the patent application “08154186.4-Method and device for removing an ionic impurity from building structures”. The new electrode units had the ability to maintain a fairly neutral to weak acidic pH in the brick during the treatment and made a desalination from a problematic chloride concentration to a very low and completely unproblematic chloride concentration possible.

During the desalination of brick masonry consisting of both bricks and mortar, crumbling of the mortar below the newly developed cathode unit was seen and further improvements were carried out. After additional improvements a pH of 7.6 in the layer which will have contact with the masonry was measured which is considered unproblematic. Application of the new (three layered) cathode unit did not result in any sign of mortar crumbling when placed at the wall section. However the final proving tests on a wall section with an applied electric field remain to be done. The improved cathode unit was incorporated in patent application “08154186.4”.

After improvement of the electrokinetic processes for desalination and dewatering, documentation of the processes and additional effects (among other neutralization effects) were carried out in laboratory scale. It was shown that desalination through electromigration is the major transport process at high electrolyte concentrations in the pore solution whereas electroosmotic water flow only is significant at low electrolyte concentrations. The concentration at which the change from desalination to water flow as domination process occurred was termed the “point of starting dewatering” and found to be 0.01 wt% chloride for the brick type Falkenløwe having $1750\text{-}1800\text{ kg} \cdot \text{m}^{-3}$ in dry density and 31-35 vol.-% in porosity. Comparison with previous results and

measurements of surface properties of different brick types (Stern layer potential found by CEC measurements) suggested that the found “point of starting dewatering” seems to be general representative in bricks and brick masonry.

During the desalination of bricks to an ion concentration below the “point of starting dewatering” the total resistance across the setup increased significantly and continually. A link between the relative increase in electrical resistance and the average water content in bricks was found. This link between the total electrical resistance across the brick and the water content made it possible to predict the actual water content in other experiments.

Electromigration in pilot scale was tested on a wall section with murals. During the 2 weeks duration, electromigration seemed efficient in areas where wetting was unproblematic - efficient both in terms of reduction of the chloride concentration in the wall and in term of the increased concentration of chloride in the poultice at the electrodes. For the areas where wetting was more problematic (wetting only possible from one of the surfaces), a lower efficiency was seen. Improvement of the wetting process in future treatments will presumably result in equally satisfying chloride reductions on large scale as seen in previous single bricks experiments.

The solubility of color pigments from murals at slightly alkaline pH is exceptionally low, and only in the case of extreme acidic or alkaline environment the solubility increases for some pigments. Since no pH changes were found in any of the brick samples as a consequence of the electric field, no pigment changes were expected in the lime layer with the pigments, and corresponding to this, no changes on the mural's surface was observed during the treatment.

The bricks used in the present study (Falkenløwe bricks) are traditionally used for restoration of historical brick masonry in Denmark and they were investigated in relation to chemical composition and pore structure.

Falkenløwe bricks of the same type and delivered at the same pallet had significant different colors and were for the investigation divided into bright, medium and dark colored bricks.

The different colored bricks variate both in the chemical composition including: the amount of soluble anion and cations concentrations, electrical conductivity and in the pore structure including: open porosity, water saturation coefficient, water absorption coefficient and also in dry density.

Chemical differences of bricks described in the literature suggest that the reason for the different red colors in Falkenløwe bricks are related to variation in firing temperature. Mainly the description of increased color intensity as a consequence of increased hematite formation by increasing firing temperature and the higher sulfate content in the bright bricks supported the hypothesis that the increasing color intensity was caused by increasing firing temperatures.

Different bricks were characterized, both regarding the amount of soluble ions and pH in relation to the influence from environmental factors (e.g. acidic rain) and firing temperatures. The environmental effect was in general found to have major influence on both the amount of soluble ions and the pH of the bricks. As expected the electrical conductivity was a good indicator for the amount of total ions and the pH measurements were shown to be a good indicator for the degree of weathering (decomposition of minerals through direct contact with the atmosphere of the planet).

The pore structure of the bricks showed relative many tiny pores for the bright red colored brick, fewer and bigger pores for the medium red colored brick, and the least and biggest pores in the dark colored red brick.

Measurement of the electrical resistance across bricks at varying firing temperatures indicates increased impedance of ion transport in bricks fired at high temperatures than in bricks fired at lower temperatures. This was related to the pore size, the distribution and the electric resistance was smallest in the bright brick with the highest number of tiny pores. The effective diffusion coefficient for dissolved salt (ions) decreased from the bright, to medium to dark colored bricks.

On basis of the investigations ion transport processes in historic brick masonry seems less predictable than in modern masonry, as variations of the pore structure occur within the structures. This is e.g. supposed to result in a higher deviation by simulation of processes in historic brick masonry with analytical models than in modern brick masonry.

The salt induced deterioration process in praxis was investigated at the vault of the so-called Birdsroom in the Carmelite Monastery (Vor Frue Monastery) in Helsingør, Denmark by SEM-EDX analysis. A location which could be subject for future electrochemical desalination of a masonry with murals.

The investigations showed sulfur along the fractures at all the measured positions whereas the sodium chloride content was relative low in these positions and contrary located in the middle of the cross sections. The found sodium chloride contents were relative high whereas the sulfur contents were low.

It was suggested that the presence of sodium chloride for several centuries combined with sulfate from the bricks, carbonate from the lime mortar, accelerated gypsum formation through repeating dissolution-crystallization cycles had resulted in the surface deterioration of the birds' room at Vor Frue Monastery in Denmark. These results underline the importance of identifying the contaminating ions and not only to focus on total concentrations.

During the examination of the content of soluble ions in new bricks, significantly higher sulfur concentrations were found for bright, poorly fired red bricks than for medium and dark colored bricks. Since presence of even low sulfur contents resulted in surface deterioration of the vault in the Carmelite Monastery in Helsingør, Denmark it should be considered whether replacement of deteriorated bricks with new bright poorly fired red bricks is appropriate.

Further developments of poultice for electrochemical removal from bricks

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Abstract

Salt induced deterioration of buildings is a frequently present problem and is in connection with new buildings a source for increased maintainness and costs. Especially in connection with Cultural Heritage (e.g. murals) deterioration of original materials is unacceptable and should be hindered. Previously, an electrokinetic method has been adapted and optimized for desalination of brick masonry and a high efficiency was obtained. Unfortunately, crumbling of mortar was observed under the cathode unit and further developments were needed.

The present paper reports development of and tests with a new type of layered cathode poultice. It was tested in acid-diffusion experiments regarding its ability to hinder acid diffusion and its ability to remain a coherent system to ensure electric contact in plastic tube tests. The pH changes throughout the experiment were followed with acid-base color indicator in the multilayered poultice. The tested cathode unit consisted of: electrode, kaolin clay, buffer components in two layers and with or without a neutral poultice layer and with or without paper between the layers.

A three layered poultice with paper between the layers showed the best results. At the bottom of the cathode unit (which is to be placed on the masonry) pH was 7.6 and this must be considered as unproblematic. An electrode unit with the layered poultice was placed at a wall section for 11 days and the mortar stayed intact. The new cathode unit seemed satisfying, however, final approval must be carried out in tests where current is applied.

Keywords

Layered cathode poultice, pH stability, acid-base color indicator, acid diffusion

1. Introduction

Electrokinetic desalination and dewatering has been known for decades. Optimization of the electrokinetic efficiency for salt removal from bricks has recently been carried out [Rörig-Dalgaard & Ottosen, 2008] with highly encouraging results and the method has potential to significantly influence future preservation and maintenance of historic structures and dwellings. Electrokinetic induced adverse effects as large pH changes at the electrodes have been neutralized by introducing buffer components to the poultices [Rörig-Dalgaard & Ottosen, 2008] which is new in comparison to previous investigations [Demberger, 1999], [Auras & Melisa, 2002], however, the neutralization needs further optimization at the cathode to avoid pH changes in the masonry next to it. Crumbling of mortar underneath the first tested cathode poultice was observed. Also changes in the brick matrix were seen. These material changes are unacceptable and further developments are needed to prevent H^+ from the cathode buffer component which is acidic acid (CH_3COOH) to enter the mortar or the brick. This was the object of the present chapter. The new idea is to introduce at least one extra poultice layer between the cathode poultice and the underlying brick and mortar for immediate neutralization of possible diffusing acid before it reach the underlying material. In the present paper both a two and a three layered cathode poultice were tested. Focus was laid on ability to hinder pH changes at the poultice surface to be attached to the masonry. Tests with different compositions of layered poultice were carried out and evaluated with acid-base color indicator. Further it was important to avoid formation of air voids through the poultice between the layers. The best composition of poultice layers was tested by placement on a wall section to observe effects on the mortar.

2. Theory

2.1 Diffusion

The diffusive flux in free solutions is in Fick's first law described as [Laidler et al., 2003]:

$$J = -DA \frac{\partial c}{\partial x}$$

Where D is the diffusion coefficient, A the area through which the ions cross and $\partial c / \partial x$ is the concentration gradient of the solute. This clarifies that increased diffusion flux occurs, both by increasing ionic diffusion coefficient and increasing electrolyte concentration.

2.2 Neutralization by use of a buffer component

The ability to oppose changes in pH by addition of acid or base is a so-called buffer action [Atkins, 1990]. The total capacity of the buffer component and thereby neutralization time is dependent of the buffer components capacity.

To neutralize the H^+ from CH_3COOH , carbonate was used in the present work as in [Rörig-Dalgaard & Ottosen, 2008]. During reaction between $CaCO_3$ and acid (H^+),

CaCO_3 decomposes ($\text{CaCO}_3 + \text{H}^+ \leftrightarrow \text{HCO}_3^- + \text{Ca}^{2+}$, $2\text{HCO}_3^- + \text{Ca}^{2+} + \text{CO}_2(\text{g}) \leftrightarrow \text{H}_2\text{O} + \text{CaCO}_3$) [Appelo & Postma, 1993].

This means that by use of buffer components for neutralization of a concentration induced diffusion of acid or base equal concentrations of buffer components and diffusing ions are needed.

3. Improvement of the cathode unit

The previous experiments with the first developed anode unit did not lead to any problematic observations [Rörig-Dalgaard et al., 2008] and no additional developments were needed. Improvements were however needed for the cathode unit due to damage of the mortar and bricks.

Acetic acid (CH_3COOH) was used as buffer component in the first cathodes [Rörig-Dalgaard & Ottosen, 2008]. The pK_a value of acetic acid is 4.7 and the buffer capacity between pH 3.8 and 5.8. [Chang 2005], [Helt 1991] and this was too acidic for the masonry. The only transport of H^+ ions from the acetic acid into the masonry from the cathode unit must occur through diffusion since electromigration transports H^+ in the opposite direction.

The new idea was to hinder this acid diffusion by placing the alkaline clay layer developed for poultice at the anode [Rörig-Dalgaard & Ottosen, 2008] between the acidic acid clay and the underlying brick and mortar. The advantage of the previously developed alkaline clay consisting of kaolin clay, calcium carbonate and distilled water was, that calcium carbonates solubility is very low and therefore undissolved in distilled water and first by acid influence it is dissolved into calcium and carbonate where the carbonate neutralize the acid at simultaneously decomposition.

4. Experimental

4.1 Analytical

The clay from the layered cathode poultice was separated in their original layers (alkaline, neutral and acid layers), dried at 105°C until equilibrium weight (24 hours) and manually crushed. 5.00 g dry clay was mixed with 12.50 ml distilled water and agitated 24 hours on a shaking table since this gave the most representative results [Rörig-Dalgaard & Ottosen, 2008 B] and the pH measured subsequently.

4.2 Basic electrode unit

From previous experiments three different clay types have been introduced. Neutral clay (consisting only of kaolin clay and distilled water), an acidic cathode clay (consisting of kaolin clay and acidic acid) and an alkaline clay (consisting of kaolin clay, calcium carbonate and distilled water).

4.3 Setup

In order to follow the diffusion of H^+ from the acidic acid layer into the alkaline layer, an acid-base color indicator was added with the relevant pH interval. An acid-base indicator is e.g. a weak acid with a distinct different color than its conjugated base.

Below pH 5-6 calcium carbonates decomposes ($\text{CaCO}_3 (\text{s}) \rightarrow \text{CO}_2 (\text{g}) + \text{CaO} (\text{s})$), meaning at least pH changes to below 6 is of relevance. Methyl red has a pH change between 4.2 and 6.3, over which the color changes from the base color (yellow) to the acid color (red) [Chang, 2005]. This means that a color change initiates at pH 6.3 as needed and methyl red was used for the present tests.

Provided a smaller pH reduction is necessary to avoid crumbling, Bromothymol blue with the pH range 6.0-7.6 could be useful. The different clay mixtures were filled into plastic tubes (4 cm in diameter, 5 cm high) in layers (two or three layers).

From the top acidic clay was placed with an ability to buffer OH⁻ formation for 2 weeks with an applied current of 2.85 mA/cm, calculated as described in [Rörig-Dalgaard & Ottosen, 2008]. Below this was the alkaline layer with a total concentration carbonate corresponding to the total concentration of acidic layer to ensure absolute hindering of the acidic front to the substrate (meaning that in worst case all the added alkaline clay was neutralized by the acidic clay).

By preliminary tests the direct contact between alkali clay and acidic clay resulted in neutralization to a high extend and formation of resistance inducing air voids. Therefore separation of these two layers (acidic clay and alkali clay) was attempted by introducing a third layer (neutral) in between and by introducing a thin diffusion open paper which previously has been used in connection with desalination with compress plaster.

4.4 Test overview

The standard with one layer acidic clay in contact with one alkaline layer was tested (2L-P). Also the effect of a porous paper to avoid direct contact between the acidic and the alkaline layer was tested (2L+P). Additional introduction of a neutral clay layer in between the acidic and alkaline clay was tested (3L-P). Finally use of both a neutral clay and porous paper for separation between the alkaline and acidic clay layers was tested (3L+P). An overview of the tests is shown in table 1.

Table 1. Test overview.

| Tests | Upper layer | Middle layer | Lower layer | Use of porous paper |
|-------------------------|-------------|--------------|-------------|---------------------|
| 2 layer –paper (2L -P)* | Acidic acid | - | Carbonate | - |
| 2 layer + paper (2L +P) | Acidic acid | - | Carbonate | + |
| 3 layer – paper (3L –P) | Acidic acid | Pure kaolin | Carbonate | - |
| 3 layer + paper (3L +P) | Acidic acid | Pure kaolin | Carbonate | + |

*L means layer and P means paper. E.g. 2L –P means 2 layered poultice without paper in between.

5. Results and discussion

5.1 Acid-diffusion experiments

The effect of the acid-base color indicators on kaolin clay was tried before the acid-diffusion experiments were initiated, figure 1.



Figure 1. The acid-base color indicator change in kaolin clay from beige (left) at pH above 6.3 to red (right) at pH below 6.3.

The ability of the multilayered clay to prevent acid diffusion to the lowest layer and minimizing volume decrease and thereby air voids was tested. Neutralization of the diffused acid into the alkaline clay results in a change from the solid CO_3 to CO_2 gas resulting in disconnections at the interface between the different types of clay layers. The clay layers were filled into clear plastic tubes and visual changes were followed during the test. After 11 days contact, the test was ended. An acidic front at the top of the alkaline layer was visible since the color had changed from the beige base color to the red acidic color, figure 2.

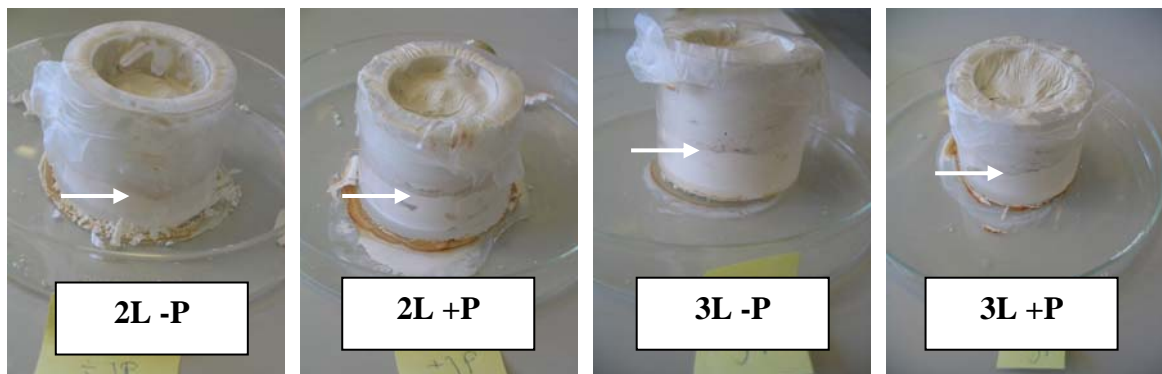


Figure 2. After ended experiment (11 days) color changes were observed in the top of the alkaline clay where the acid-base color indicator was added (white arrow).

Air voids were present to varying extends. Such disconnections will have a negative influence on the electrokinetic treatment as air voids results in increased resistance. The total volume of the air voids were estimated for the different tests by pressing the clay together from the top and measuring the volume reduction. A reduction in the total poultice layers was seen (figure 3) and measured before the plastic tubes were removed from the clay poultice to:

- 2L -P: 1-1 ½ cm
- 2L +P: ½ cm
- 3L -P: 3 mm
- 3L +P: 1mm



Figure 3. Visible variation in the height after ended tests (11 days). The highest volume decrease was seen left (2L-P) and the lowest right (3L+P). The dotted white line indicates the initial height, however minor visual changes happened during the plastic tubes were removed.

Due to small color variations between the alkaline, neutral and acidic clays it was possible to see, that the volume reduction mainly occurred in the alkaline layer, most probably during the neutralization of the diffused acid. The observed differences with and without paper between the layers indicates, that direct contact between the acidic and the alkaline clay results in increased reaction between the layers.

Based on these tests with layered poultice, the 3 layered model with paper between the different layers seemed to result in the most satisfying results.

Besides the acid-base color indicator, traditional pH measurements were carried out, table 2.

Table 2. pH measurements in the different clay layers.

| Experiment | + | +/- layer | - layer (upper) | - layer (lower) |
|-------------------------|-----|-----------|-----------------|-----------------|
| 2 layer – paper (2L -P) | - | - | - | - |
| 2 layer + paper (2L +P) | - | - | - | - |
| 3 layer – paper (3L -P) | - | - | - | - |
| 3 layer + paper (3L +P) | 6.1 | 6.1 | 7.5 | 7.6 |

- Not measured

Kaolin clay with distilled water has a pH of 8.8. Initially the pH in the anode clay was 8.6 and 4.4 in the acidic acid clay.

5.2 Test of the new layered cathode poultice

In Rörig-Dalgaard et al. (2008) electrokinetic desalination was carried out with the previously developed buffer poultices. The pH measurements made of the samples from the wall section showed no significant change, however crumbling of the mortar was observed. It is therefore most likely that the lime mortar worked as a buffer. Therefore solely pH measurements of the samples from the wall section are insufficient for evaluation of the new improved cathode poultice. The three layered cathode poultice with paper was placed at the same wall section as used in Rörig-Dalgaard et al. (2008) for the same 2 weeks and possible crumbling was observed visual.

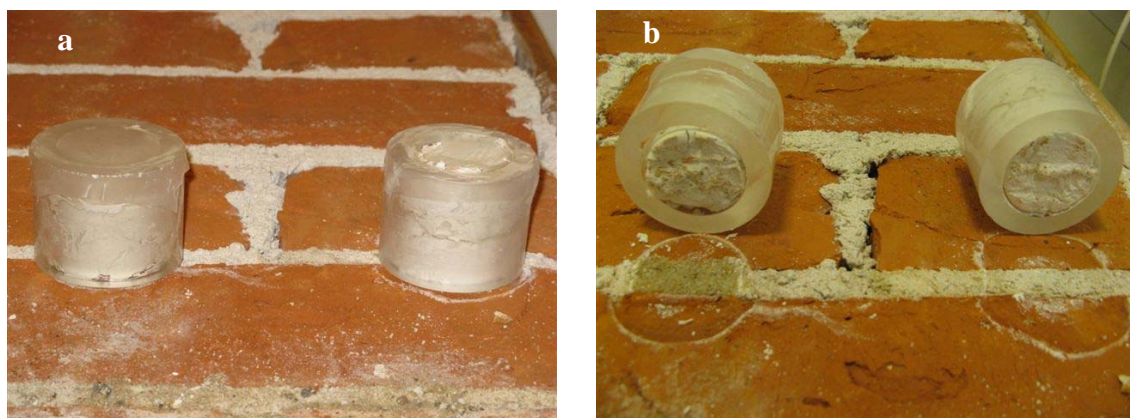


Figure 4. Tests of the newly developed three layered cathode poultice right compared with the previous cathode poultice (solely consisting of acidic acid clay) left. (a) The plastic tubes were placed just above the mortar (mortar crumbling in the lower parts of the picture induced by a previous cathode unit) (b) Effect on the mortar after 11 days contact with the poultices. Crumbling left no visual changes right.

In figure 4 (b) left, the one layered cathode poultice showed the same extend of mortar crumbling as seen in previous experiments, contrary the newly developed three layered cathode poultice did not lead to any change of the mortar. The two visible white rings in figure 4 (b) right are small leftovers of harmless clay.

Comparison of the effect from the cathode poultice on the mortar between the one layered and the three layered cathode poultice shows significant progress and it seems like the necessary improvements have been obtained before use of the poultice during electrokinetic desalination of Cultural Heritage buildings.

6. Conclusion

In this paper prevention of acid diffusion from the cathode poultice into the underlying brick and mortar was aimed. Use of several layers (two or three) at the cathode unit prohibited the acid to spread through diffusion. The acidic front was followed using an acid-base color indicator and in the two layered poultice without paper between the layers several mm acidification of the carbonate enriched kaolin clay was seen. These observations were supported by traditional pH measurements. The experiments showed that use of a three layered cathode unit with paper in between the layers hindered acid diffusion and a pH of 7.6 in the layer which will have contact with the underlying brick and mortar is considered unproblematic. Application of the new three layered cathode unit did not result in any sign of mortar crumbling when placed at the wall section. However the final proving most occur by tests on a wall section with an applied electric DC field.

The improved cathode unit is incorporated in patent application 08154186.4-Method and device for removing an ionic impurity from building structures.

7. Future investigations

7.1 Test of the layered cathode poultice during electrokinetic desalination.

The observed crumbling of the mortar seen in Rörig-Dalgaard et al. (2008) was presumed to be caused by diffusion of the H^+ from CH_3COOH at the cathode. The acid-diffusion was hindered after the present improvement of the cathode poultice. However, this claim should be tested by application of the new cathode unit at a wall section with bricks, mortar and an applied current. Again changes during the treatment should be followed by use of acid-base color indicator like in the acid-diffusion tests.

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