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Influence of Brick Properties on Salt Crystallization Damage

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Abstract

The quality of the materials constituting masonry has a major influence on the type and seriousness of the damage that can occur due to salt crystallization. In the case of brick, the composition of the original clay, together with the production process, determine the quality of the final product and its eventual susceptibility to salt decay.

The paper describes a case study where different bricks, exposed to the same environmental conditions, show a considerable difference in their resistance to deterioration by salt crystallization. Using the condition survey of the church tower in Oostkapelle, the possible relation between the damage and the physical and chemical properties of the bricks was investigated. Bricks showing very serious damage (orange bricks) as well as bricks showing no damage (purple bricks) were sampled and characterized mainly by polarization and fluorescence microscopy. The type and the quantity of salts present in the different bricks were also investigated. The observed damage was evaluated in the light of the results obtained from the analysis performed and a relation between the quality of the original material and the firing conditions of the brick to its susceptibility to salt decay could be drawn.

Keywords: brick, salt crystallization, polarized fluorescent microscopy,

Einfluss der Eigenschaften von Ziegeln aus gebranntem Ton auf den durch Salzkristallisation hervor gerufenen Schaden

Zusammenfassung

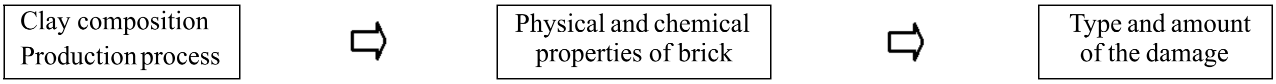
Die Qualität der Bestandteile eines Mauerwerks hat einen entscheidenden Einfluss auf Art und Ausmaß des Schadens, der durch Kristallisation von Salzen hervorgerufen werden kann. Im Falle eines Ziegels aus gebranntem Ton bestimmen die mineralogische Zusammensetzung des verwendeten Tons und der Herstellungsprozess die Qualität des Endproduktes und seine Empfindlichkeit gegen zerstörende Salzeinwirkung.

In diesem Beitrag wird eine Fallstudie beschrieben. Dabei wurden unterschiedliche Ziegelsteine ein und denselben Umgebungsbedingungen ausgesetzt. Sie zeigten ein stark unterschiedliches Verhalten bezüglich der Widerstandsfähigkeit gegen Zerstörung durch Kristallisation von Salzen. Eine Zustandsüberprüfung des Kirchturms in Oostkapelle (Niederlande) wurde dazu benutzt einen möglichen Zusammenhang zwischen dem aufgetretenen Schaden und den physikalischen und chemischen Eigenschaften des Ziegels zu untersuchen. Ziegel, die starke Schäden aufwiesen (orangefarben) einerseits und Ziegel, die unbeschädigt blieben (dunkelrot) andererseits wurden entnommen, um sie in erster Linie mit Hilfe der Polarisations- und Fluoreszenzmikroskopie charakterisieren zu können. Die Art und die Menge der Salze in den unterschiedlichen Ziegeln wurden ebenfalls bestimmt. Der beobachtete Schaden wurde auf der Basis der mit Hilfe dieser Analysen gefundenen Ergebnisse interpretiert. Es gelang eine Beziehung zwischen dem Rohmaterial und den Bedingungen beim Brennen der Ziegel mit deren Empfindlichkeit gegenüber Salzeinwirkung herzustellen.

Stichwörter: *Ziegelstein, Salzkristallisation, polarisierte Fluoreszenzmikroskopie.*

1 Introduction

The damage that can occur due to salt crystallization is strongly influenced by the quality of the materials constituting the masonry. Physical properties such as porosity, pore size distribution, water absorption and drying behaviour, as well as chemical and mineralogical properties (composition) of the building materials, play a fundamental role in the risk of failure of the material over time. In the particular case of bricks, the composition of the original clay together with the production process, especially the firing temperature, determine the quality of the final product and therefore the susceptibility of the material to the salt crystallization mechanism. The type of damage that occurs to bricks in service can be properly explained if the physical and chemical properties of the bricks are related to the composition of the original clay and the production process of the brick.



In the following paragraphs damage caused to fired-clay brick by salt crystallization is considered. For this purpose, a case study is presented in which different bricks, exposed to the same environmental conditions, show a considerable difference in the extent of the decay.

2 Case Study

The study object was the tower of the church in Oostkapelle, in the province of Zeeland, in the south west of The Netherlands. This province was flooded by the sea several times over the centuries. The last severe flooding took place in 1953. The tower (Fig. 1), erected at the end of the 14th century, is the most ancient part of the church. Although the water did not reach the church and the tower during the flood, thanks to their position on an artificial slope, a high sea salt concentration is supposed to be still present in the soil. Therefore, after 1953 sea flooding the tower underwent a last restoration in 1954-57.

The most serious damage is visible on the west side of the tower, at a height of about 3-4 m where the mortar has been completely lost and the bricks fall apart. In all the affected parts of the tower, a difference in damage can be noticed between the darker (purple) and the lighter (orange) coloured bricks: the first showing no damage, the second suffering powdering and erosion (Fig. 2, 3).

2.1 Analyses and Results

The aim of the research was to determine the cause of the damage and to explain the differences in decay found on the different types of bricks composing the masonry.

The age of the building and its location near the sea suggest that the causes of damage could be related to the flooding incidents and the salt spray. In order to investigate the mechanisms of damage in detail, drilling powder samples were obtained from different depths of damaged (orange) and undamaged (purple) bricks and the hygroscopic moisture content (HMC) at 96 % RH was determined. The HMC measurement [1] is based on the fact that materials

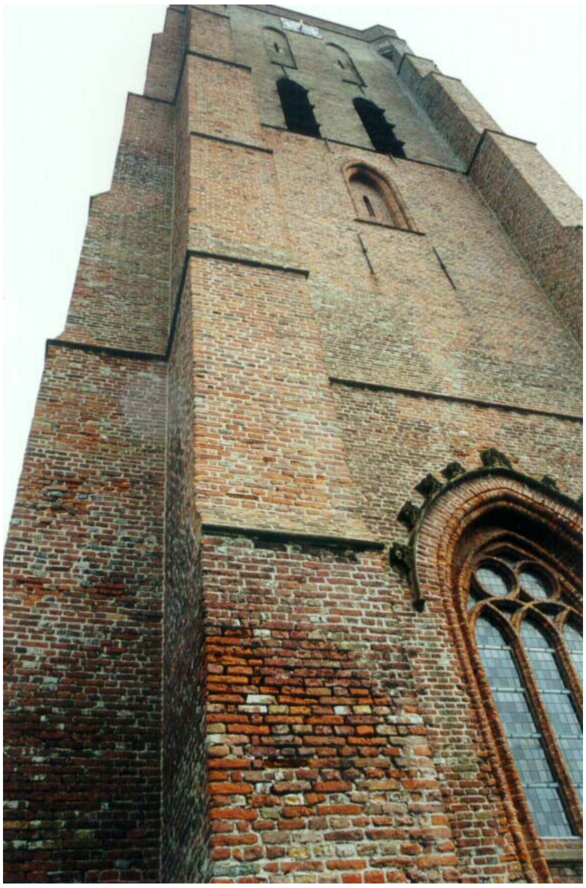


Figure 1: Tower of the church of Oostkapelle

Figure 2: Damage occurring on the west wall of the tower

contaminated with hygroscopic salt (for example NaCl) are able to absorb moisture from the air if the RH of the air is higher than the equilibrium RH of the salt (75.5 % in case of NaCl [2]). The HMC is not a quantitative method, but gives a fairly good indication of the presence of hygroscopic salts. The results obtained in this case are reported in Fig. 4. The purple brick had very low hygroscopic moisture content, while the orange brick showed a high hygroscopic moisture content decreasing slightly from the surface towards the interior of the brick. From the high values of the HMC measured in the orange brick, hygroscopic salts, like NaCl, are supposed to be present. To verify this hypothesis chemical analyses were performed on the powder sampled from the orange brick and the Cl^- and SO_4^{--} content was determined. The Cl^- content was determined by acid digestion with nitric acid (2,8 M HNO_3) followed by titration with silver nitrate ($AgNO_3$). The SO_4^{--} was precipitated as barite ($BaSO_4$) by adding $BaCl_2$ to the solution and the SO_4^{--} content was subsequently determined by flame spectrometry.

The results are reported in Fig. 5 together with the values of the HMC. A high Cl^- content is present throughout the brick and it is likely that these ions are combined with Na^+ to form sodium chloride. This salt could well be at the origin of the observed high values of HMC. The source of sodium chloride is most probably sea salt spray considering the short distance from the sea (about 2 Km), the orientation of the wall (W) and the main wind direction (S-W). Furthermore, at the height where the sampling was performed, no rising damp was present. The chloride content is almost constant in depth up to 10 cm from the surface showing that sodium chloride can easily penetrate in very porous material up to considerable depths. From the chemical analyses also sulphate ions appeared to be present in the brick: their quantity decreases towards the inside of the wall suggesting their external source. The different distribution between chlorides and sulphates is related to their different solubility: the more soluble chlorides can easily penetrate in depth, whereas the less soluble sulphates stay on the surface [2,3]. The contribution of the sulphates to the total HMC is clear in Fig. 5, since the Cl^- content constant, the decrease in HMC must be related to the SO_4^{--} content.

The difference in salt content between orange and purple bricks confirms that salt crystallization is the

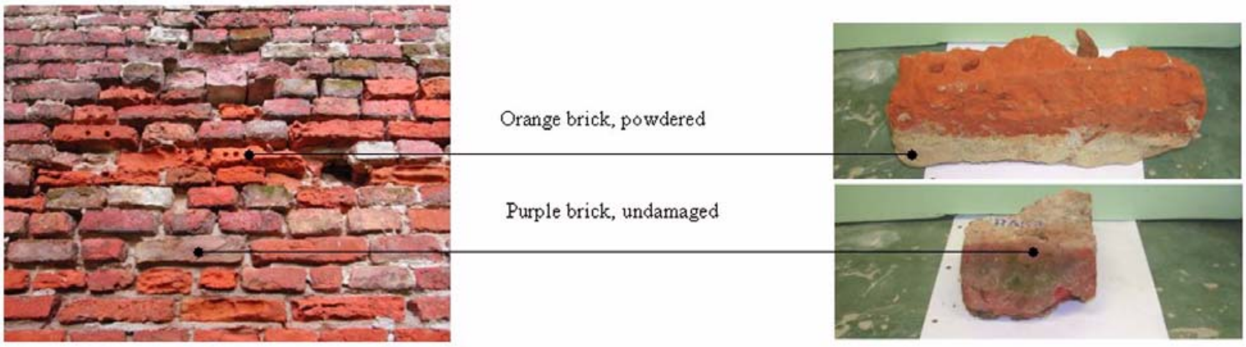


Figure 3: Damage of different seriousness occurring on orange and purple bricks

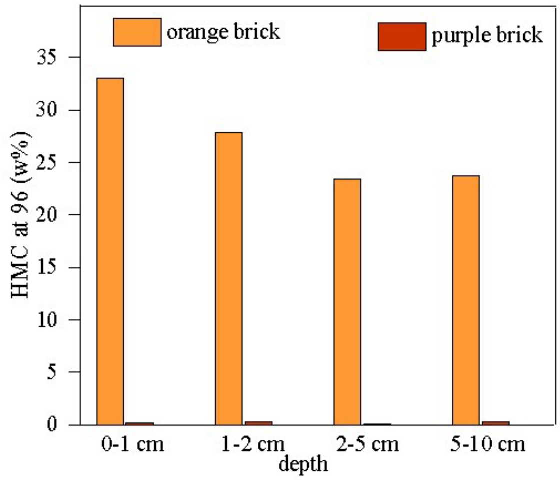


Figure 4: HMC at 96 % RH measured on orange and purple brick

main decay mechanism. However, to explain the reason for the different salt content and damage between these bricks exposed to the same environmental conditions, their physical, chemical, mineralogical and micro-structural properties have to be considered.

At first the total porosity and the density of both orange and purple bricks was determined by immersion of desalinated brick samples: these measurements showed a very high porosity (40 %) in case of the orange brick and lower values (33 %) for the purple one. However, the total porosity is not a sufficient parameter to evaluate the quality of a brick: also the pore size distribution has to be known to allow the formulation of hypotheses regarding the susceptibility of the material to damage mechanisms. The pore size distribution was measured by means of mercury intrusion porosimetry (MIP) and the results are reported in Fig. 6. The difference between the bricks is very clear:

- the orange brick has a high porosity (40 %) and very fine pores, smaller than 2 µm. A high percentage of the pores is in the range in which capillary condensation is possible (< 0.1 µm);
- the purple brick has a lower total porosity (29 %) and coarse pores, in the range of 5 up to 20 µm.

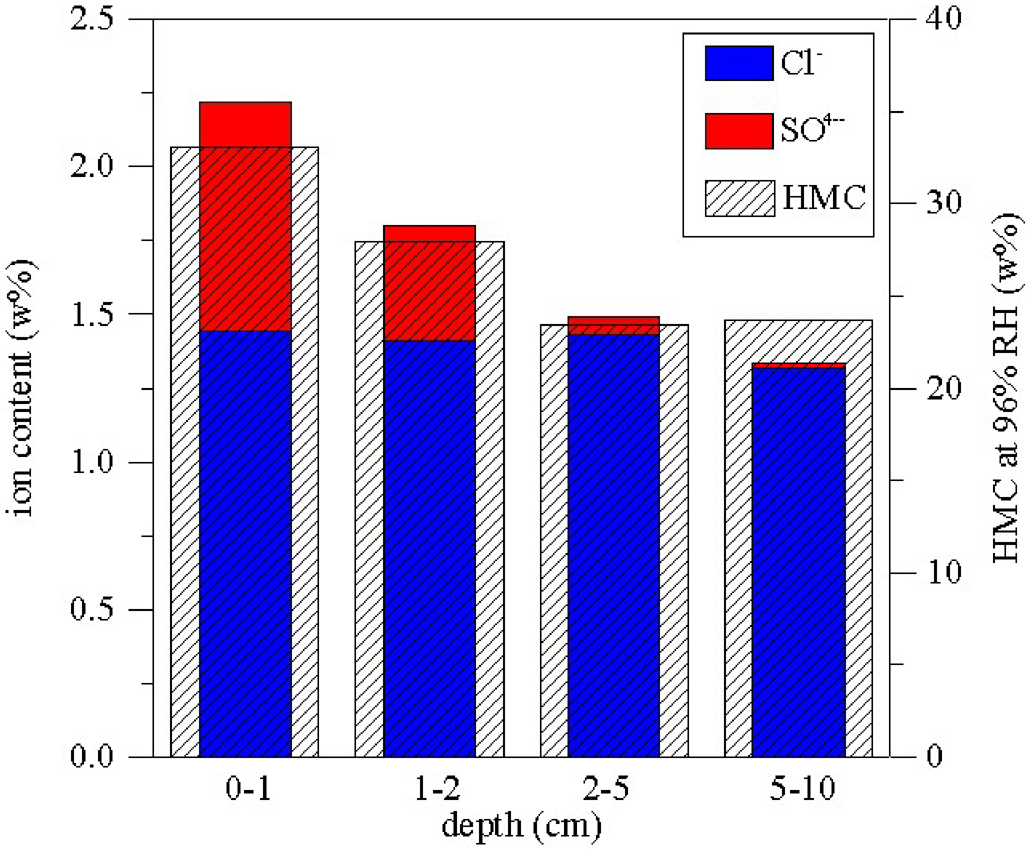


Figure 5: Cl^- and SO_4^{--} ions distribution in orange brick

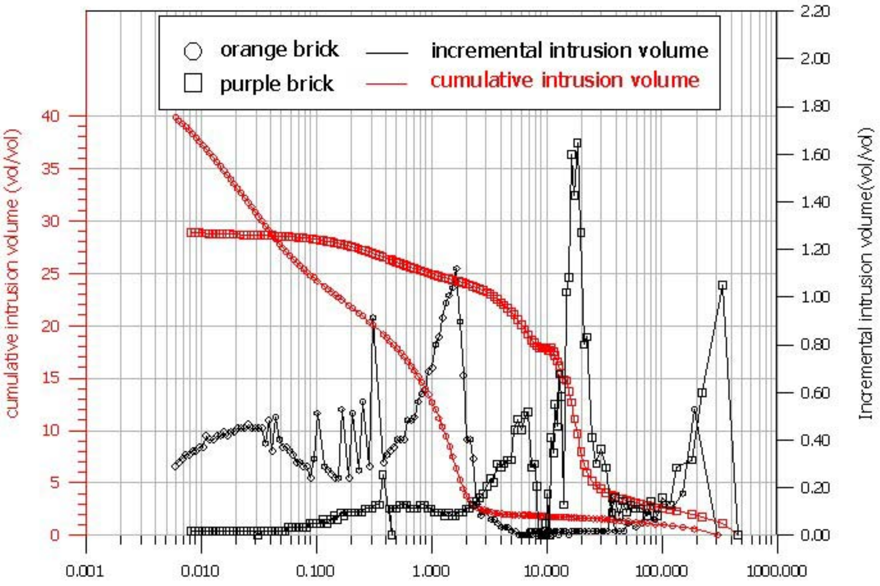


Figure 6: Pore size distribution of orange and purple brick as determined by MIP

The high porosity measured in the orange brick and the presence of very small pores can explain the considerable uptake of salt and the ensuing serious deterioration. The high porosity allows a high moisture (and salt solution) uptake; the presence of small pores slows down the drying while allowing capillary condensation at RH lower than 100 %. Consequently, the material stays wet for a longer time with all the negative consequences that this can have on the damage (susceptibility to frost damage, reduced mechanical strength, possibility of biological growth, etc.). Moreover, the presence of salts in the pores makes the material susceptible to RH changes through the crystallization and dissolution cycles occur whenever the RH of the air crosses the equilibrium RH of the salt; these cycles generate pressure in the material which, if the mechanical strength of the material is overcome, will lead to damage phenomena like powdering. Materials with a high number of pores having sizes between 0.1 µm and 1 µm, like the orange brick considered here, are more susceptible to salt damage [4, 5]. It should also be noted that a high porosity as measured in the orange brick (40 %) often corresponds to a low mechanical strength and therefore to a low resistance to crystallization pressure.

To understand the origin of the differences between the two bricks, i.e. in order to relate them to the composition of the original materials and to the production process, polarization and fluorescence microscopic analyses were performed on thin sections obtained from the orange and the purple bricks. The specimens were vacuum impregnated with a UV fluorescent resin so that the voids could easily be distinguished from the bulk material. The content of voids visible in the microscope was determined using a point-counter that had been mounted to the stage of the microscope. The purpose of the study was to determine any differences in the internal structure of the two bricks that may result from the composition of the clay and from the firing temperature. It was also important to find out if a relation between these two factors and the amount of the damage could be drawn.

Figures 7 and 8 are fluorescent photomicrographs of thin sections showing the composition of each of the bricks. Both samples consist of particles of sand, mostly quartz, with small amount of oxides embedded in a matrix of clay. A significant difference between the two bricks from the point of view of the mineralogical composition is that whereas the purple sample contains almost no carbonates, the orange sample contains a relatively high amount of carbonate in the form of calcite originally present in the clay (primary) (Fig. 8 a). A considerable portion of this carbonate has re-crystallised as shown in Figure 8 c. The source of the re-crystallized calcite is likely to be the original clay; the hypothesis of an external source (for example the mortar joint) seems to be less probable since no calcite is present in the purple brick sampled from the same wall.

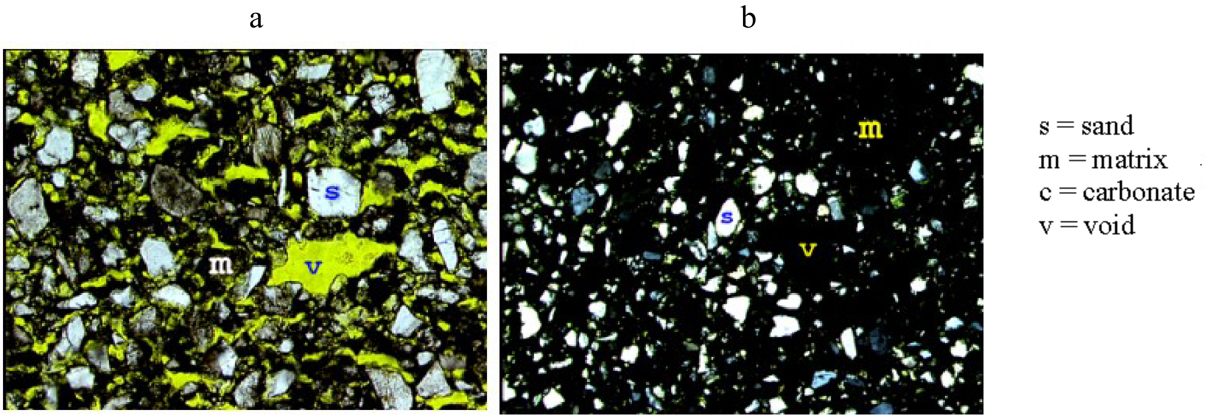


Figure 7a-b: PFM-micrographs showing an overview of the purple brick sample: the brick contains hardly any carbonate (image size: 2.7 mm x 1.8 mm)

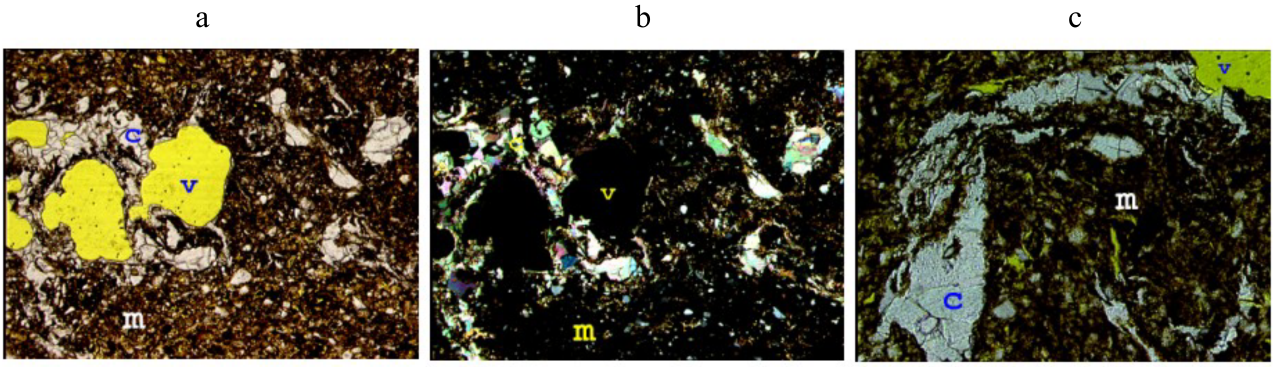


Figure 8: PFM-micrographs showing an overview of the orange brick sample: the brick contains a considerable amount of carbonates in the form of calcite (image size: 2.7 mm x 1.8 mm.). In (c) re-crystallized carbonates are visible

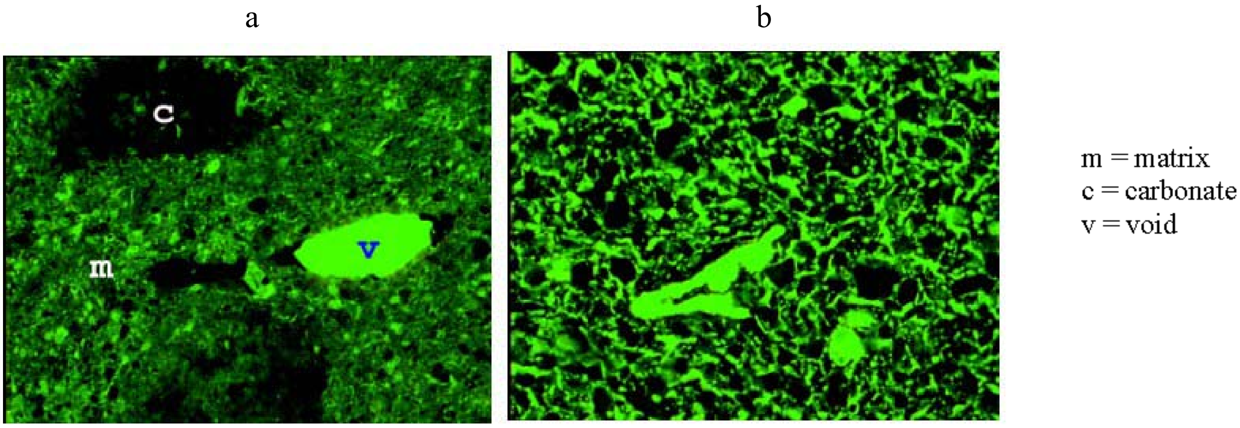


Figure 9: PFM-micrographs showing an overview of the internal structure of the two brick samples. The orange brick (a) seems to contain more of very fine pores than the purple brick (b) (image size 2.7x1.8mm).

One of the methods of determining the temperature of firing of the bricks is to determine their mineralogical composition, either by means of X-ray diffraction analysis [6] or by means of optical microscopy. In this case polarization microscopy was used. Various minerals or compounds in stone and similar materials will decompose upon heating at specific temperatures. Most carbonates, especially when existing as finely divided crystals, will decompose at temperatures higher than 650 ^{o}C. The presence of considerable amount of unaffected primary calcite ($CaCO_3$) in the orange brick is a clear indication that the firing temperature of that brick was too low; or else, assuming the firing temperature was high enough, it is probable that the duration of firing of the brick at that temperature was too short to generate the decomposition of the calcite.

The internal structure, i.e. the presence and the distribution of the voids, was studied by means of fluorescence microscopy. Figure 9 shows the fluorescent micrographs of the two bricks and it can be seen that the orange sample contains a lower amount of 'visible' voids than the purple sample. Most of the voids in the orange sample are smaller than the resolution of the microscope, i.e. < 1 μm. By means of the point counting method the voids content was calculated. The results obtained are reported in Table 1 together with the results of total porosity measured by immersion and by MIP.

The data show that the void content values obtained by means of point counting are considerably lower than those obtained by means of immersion in water or by MIP. This is due to the fact that the very small pores, varying in diameter between 0.01-1 μm, are not visible with an optical microscope. The pore content determination by means of water immersion or mercury intrusion, however, is able to measure these capillary pores. The difference between the values obtained by point counting and the other techniques is more evident in material containing a large fraction of pores smaller than 1 μm, i.e. in the orange brick.

The different pore size distribution of the two bricks can be related to the clay composition: clays containing a large amount of carbonates generate bricks with smaller pores [7] than clays with a lower content of carbonates.

Also the firing temperature can have an influence on the pore size distribution and on the total porosity. If the original clay used for both the orange and the purple brick was equal in particle size and composition (factors that in the present case cannot be determined), the higher total porosity and the larger pores of the purple brick can be explained by a higher firing temperature. In fact clay fired at higher temperature produces brick with relatively large pores and with a total porosity lower that the porosity of brick obtained from the same clay fired at lower temperature. The pore radius increases with about 0.1-0.2 μm every 100 ºC [7].

Table 1: Void content in the orange and purple brick, measured by different techniques.

Void content (% by volume)	Orange brick	Purple brick
Point counting	8	19
Immersion in water	40	33
MIP	40	29

3 Conclusions

It is common to observe differently decayed bricks on the same masonry wall of ancient buildings, in part because of the several repairs and restorations that these have undergone. Differences in damage under the same environmental conditions can often be related to the quality of the bricks. In the present research two types of brick, clearly distinguishable by their colour and the amount of the decay, were investigated: a very seriously powdering orange brick and a sound purple brick. The results of the study allowed relating the extent of the damage to the physical properties of the bricks, mainly to their water absorption, total porosity and pore size distribution.

The seriously powdered orange brick showed a high total porosity and a large percentage of small pores. Both these factors resulted in making the material more susceptible to salt crystallization damage:

- The high porosity leads to a low mechanical strength and to a high water and salt solution absorption;
- The presence of a high number of small pores leads to high water retention and to capillary condensation with all the negative consequences that this entails regarding both damaging cycling around the equilibrium RH of the salt and frost damage.

The physical properties of the bricks were related to the composition of the original material and to the production process: the use of a clay rich in carbonates and the low firing temperature contributed significantly towards the poor quality of the orange brick.

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References

1. E. De Witte et al., *Measurement techniques* in “Evaluation of the performance of surface treatments for the conservation of historic brick masonry”, EC Research Report N. 7, R.P.J. van Hees Editor, Official Publication of the EC, Luxemburg 69-88 (1998)
2. A. Arnold, K. Zehnder, *Salt Weathering on Monuments*, in Proceedings of the 8th Int. Congr. On Deterioration and Conservation of Stone, Berlin, J. Riederer Editor, 31-58 (1996)
3. F. Auger, World limestone decay under marine spray conditions, in La Conservazione dei Monumenti nel Bacino del Mediterraneo - Atti del 1º Simposio Internazionale, F. Zezza Editor, 65-69, Bari (1989)
4. R. Rossi Menaresi and A. Tucci, *Pore structure and salt crystallization: “salt decay of Agrigento biocalcarenite and “case hardening” in sandstone*, in La Conservazione dei Monumenti nel bacino del Mediterraneo - Atti del 1º Simposio Internazionale, F. Zezza Editor, 97-100, Bari (1989)
5. E. Doehne, *In situ dynamics of sodium sulphate hydration and dehydration in stone pores: observations at high magnification using the environmental scanning electron microscope*, in “3rd Int. Symp. On the Conservation of Monuments in the Mediterranean Basin”, V. Fassina, H. Ott, F. Zezza, Editors, 143-150, Venezia (1994)
6. I. Schumann Zur nachträglichen Bestimmung der Brenntemperatur und zum Einfluss der Brenntemperatur auf die chemische Beständigkeit von Ziegeln, PhD thesis, Technische Universität Hamburg-Harburg, Aachen (1997)
7. B. Fabbri., M. Dondi, *Caratteristiche e difetti del laterizio*, Faenza (1995)

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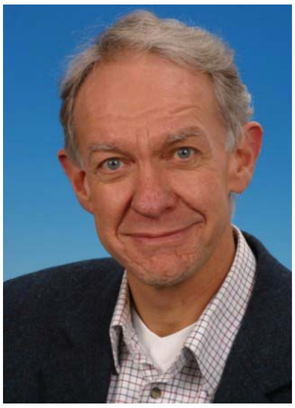

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