PAPER • OPEN ACCESS

Microstructure Ceramic Changes Resulting from Sodium Sulphate Subflorescence

View the article online for updates and enhancements.

IOP ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Microstructure Ceramic Changes Resulting from Sodium Sulphate Subflorescence

Maria Wesolowska [1]

[1] UTP University of Science and Technology in Bydgoszcz, S. Kaliskiego 7, 85-796 Bydgoszcz, Poland

marysia@utp.edu.pl

Abstract. In this article, the influence of sodium sulphate crystallization on microstructure changes in traditional ceramic was discussed. The tested elements in form of brick halves underwent capillary moistening in sodium sulphate solution with concentration of 5, 10, 15, 20, and 25%, and then their bottom walls were protected with polyethylene covers in order to ensure drying only through side walls. After drying, samples were taken from face walls (5mm) and 2 subsequent lower layers (each 10mm thick). Prepared samples were used for comparative analysis of ceramic microstructure changes caused by salt crystallization and material damage visible after salt extraction. In the tests, mercury porosimetry and confocal microscopy were used. Because of necessity to dry the samples to solid mass, the temperature of 80°±5°C was defined which enabled removing free water without damaging of crystallized salt structure. Based on the ceramic analysis, the initial salt concentration when macroscopic damage starts as a result of subflorescence (face layer delamination) was found. The analysis of pictures from a confocal microscope enabled to define the mechanism for ceramic material damage. A characteristic granular diffusion was observed which is the effect of pushing out ceramic by building out the sulphate crystals.
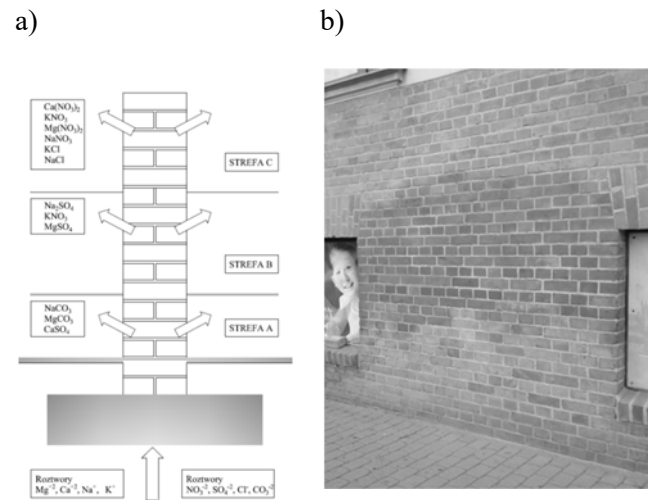
1. Introduction

Subflorescence is defined as a potentially harmful accumulation or salt deposit layer under wall surface, resulting from moisture evaporation from the wall [1]. The phenomenon intensifies during freeze-thaw cycles when the mixture of humidity and salt freezes and expands, creating internal pressure which with a necessary value can split a part of the wall in external areas or cause its delamination [2]. The subflorescence process is possible when the following (simultaneous) conditions are fulfilled [3]:

- there is a source of water soluble salts (mortar components, atmosphere, ground, metal and other elements built in the wall),
- the wall is penetrated by water in which salts will be dissolved,
- there is a factor causing movement of salt solution (difference of concentration, temperature or pressure between wall interior and its surface).

Additional factor which needs to be considered in analysing the subflorescence causes is the time of water contact with a salt source. If there is a source of salt in the wall that dissolves well in water (for instance sodium chloride $NaCl$ or sodium sulphate Na_2SO_4), then even a short period of water contact (for example a short rain) can result in a solution with a high concentration of salts, their

transport through porous material and accumulation of the crystallizing salt at the wall surface. The content of salts crystallized in the wall depends on their solubility (Figure 1).

a)   b)

Figure 1. Salt crystallization in a wall: a) crystallization zones by Rokiel [4], b) salt presence effect in a real object
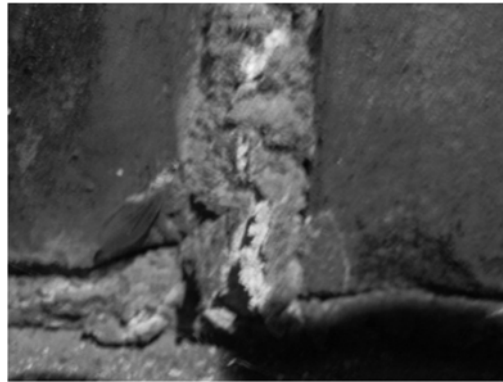
Salt solutions can crystallize in:
- a subsurface layer of ceramic (in cracks and pores) - lenses and concentrations made of salt crystals called subflorescence or crypto-florescence are formed (Figure 2),
- closed spaces between wall components–then the wall is blown apart (Figure 3).

Pel and others indicate that salt concentration occurs mainly in the subsurface reaching about 25mm [5]. The aim of the work is to define the influence of sodium sulphate subflorescence (Na_2SO_4) on changes in the ceramic microstructure and definition of salt concentration which initiates this phenomenon.
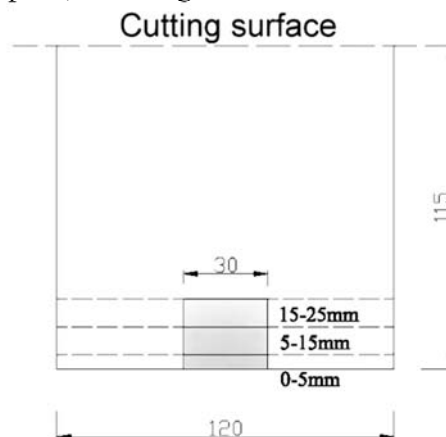

Figure 2. Subflorescence effect in a face brick in lens-shaped forms of sodium chloride

Figure 3. Subflorescence effect in a joint of a wall made of ceramic elements

2. Research Procedure

For the tests, 36 samples sized 120x115x60 mm were used, made from red ceramic with the apparent density of 1660kg/m^3. Five groups with 6 samples each were capillary moistened with sodium sulphate solution of concentration at 5, 10, 15, 20 and 25%. The rest of the group was an initial sample marked as 0%. After moistening to a solid mass, the top and bottom surfaces were protected with a polyethylene screen such that drying occurred only by side surfaces. The drying period was 10 weeks. Next, 3 layers were chipped off from each sample according to the scheme showed in Figure 4. Precise chipping off was ensured by a special insert for a universal testing machine equipped with metal blades (bottom – fixed with side guides enabling sample movement and top guides – movable). Each part was divided into two parts, one designed for tests and the second for salt extraction.

Figure 4. Diagram of the sample material selection for microstructure tests

Prepared single fragments with amass of 5g were combined into one general sample. In order to extract the salt, the general samples were put into containers of 2000 cm^3, immersed in distilled water in proportion 1:50 and left for 24 hours in normal conditions. This process was repeated 5 times. Next, the samples were dried to a solid mass. Taking into account the properties of hydrated sodium sulphate (during warming it dissolves in its own crystal water at about +32°C, and when reaching about +100°Cthe water from the compound evaporates and creates anhydrous sodium sulphate - thenardite, Na$_2$SO$_4$), samples were grouped in the containers and dried at +80±5°C. After being taken out from the drier, they were cooled in an exsiccator and weighed after reaching 30 °C to 40 °C. Prepared general samples were sorted for laboratory tests. Immediately before porosimetry tests, the samples were weighed with an accuracy of 0.01g and placed in a penetrometer.

For definition of microstructure parameters and porosimetry distribution, the mercury porosimetry was applied [6]. The measurements were performed with the Autopore 9220 in the range of pressure from atmospheric to 414 MPa, which allowed to measure the volume and distribution of pore sized in the radius range of 313 000 nm to 4nm. According to the IUPAC classification [7], the distinguished range includes: macropores (pore diameter 313 000 – 50nm) and mesopores (pore diameter 50 – 2nm). Out of the measurement range, there are mesopores with the smallest sizes and micropores (<4nm). The capillary flow occurs mainly in pores with diameters of 300 – 3 000 nm. The remaining pores determine the capillary flow in much less rate (because of the essential influence of friction forces or gravity forces) [8].

Except for pore size distribution which was based on porosimetry analysis, the material density in mercury at pressure of 0.1MPa and 414MPa was defined. At pressure of 0.1MPa, mercury does not penetrate into the sample interior, but only washes it so the measured value is the volume density. Under pressure of 400 MPa, mercury can penetrate pores wider than 4 nm in a material, so the measured value dP is density which considers pores smaller than 4 nm.

With measurements by a porosimeter, the following microstructure parameters were defined: mercury intrusion, total pore volume, density and volume density of the material, logarithmically differential pore volume distribution.

The pore volume responsible for capillary flow was calculated from the formula:

$$U_{cap} = \frac{\sum_{i=300nm}^{3000nm} IV_{cap}}{TIV} \cdot P$$

(1)

where:
IV_{cap} – mercury intrusion in the range of diameters 300-3000nm,
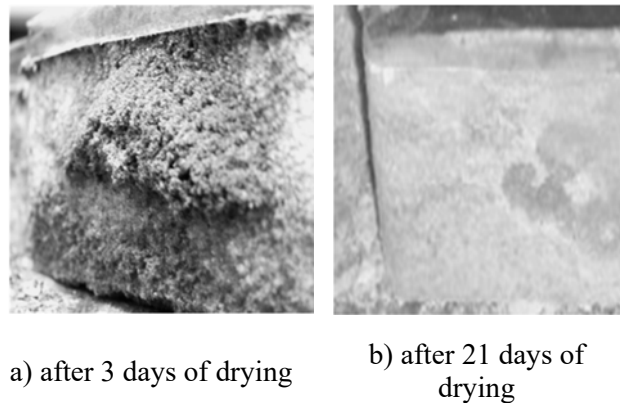TIV – total mercury intrusion,
P – open porosity, %.

To illustrate the destruction range of the material microstructure, confocal microscopy was used. The confocal microscopy is a variation of a light microscopy characterized with enlarged contrast and thus definition. Light which is stimulated in points lying outside focus is eliminated by a pinhole system (hole lens) and does not take part in picture creation. The result is a 3D picture which does not contain composites from other planes than the focal one.
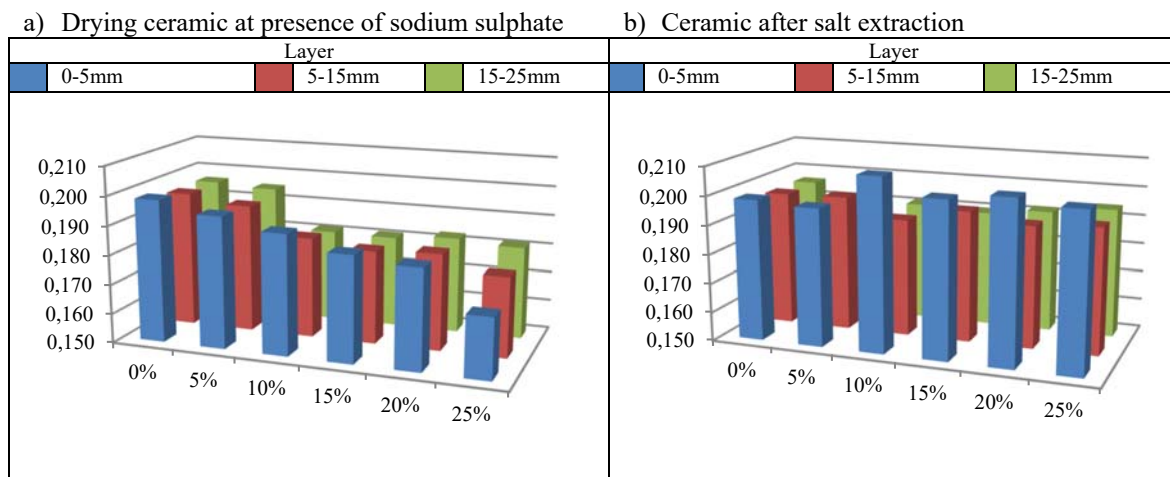
3. Test results and discussion

During the drying of wall ceramic elements in presence of sodium sulphate it was found that the damaging processes of ceramic material occur from the beginning of the drying. Ceramic material is destroyed and pushed out on the surface with crystallizing salt creating large needle-like efflorescence. After some time, efflorescence with ceramic particles changes into a dense deposit described in [9] (Figure 5). During drying, this dense deposit comes off. At the extraction of salts, the flat ceramic fragments delaminate.

In the course of porosimetry tests for divided ceramic layers, density, volume density and the volume of mercury pressed into the samples were defined. The results are presented in Table 1 and Figure 6.

The results presented indicate the lowering of the specific weight for the samples dried in presence of sodium sulphate. It is caused by depositing of sulphate in the ceramic structure whose density is 2.32g/cm^3 [8]. For the salt concentration up to 15%, the filling of crystallizing sulphate is visible. However, at higher condensations the salt crystallizes on the surface and in subsurface zone (5-25mm). The salt crystallizing effect is visible in mercury intrusion amount (Figure 6).

a) after 3 days of drying   b) after 21 days of drying

Figure 5. Crystallization of sodium sulphate during the drying of samples

a) Drying ceramic at presence of sodium sulphate   b) Ceramic after salt extraction

Figure 6. Mercury intrusion into ceramic samples

Table 1. Basic parameters of ceramic microstructure

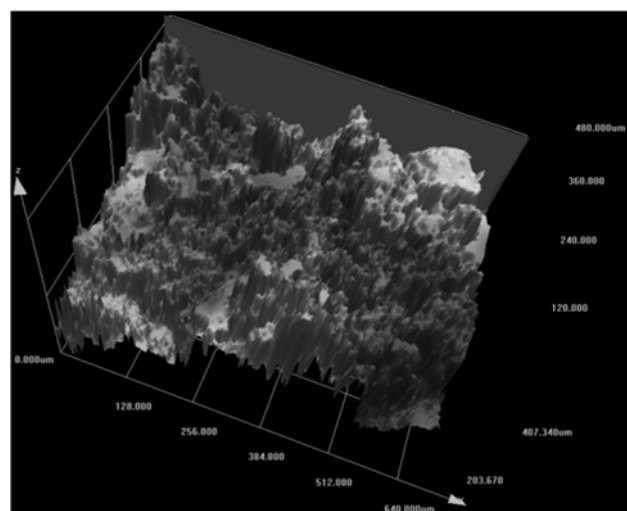| Concentration of Na_2SO_4		Density g/cm^3		Volume density g/cm^3		Pore surface m^2/g	
		I	II	I	II	I	II
0	0-5mm	2.52		1.68		28.44	
	5-15mm	2.49		1.67		28.47	
	15-25mm	2.49		1.67		27.92	
5%	0-5mm	2.50	2.52	1.68	1.62	1698	26.50
	5-15mm	2.47	2.49	1.67	1.66	12.58	16.33
	15-25mm	2.47	2.47	1.67	1.68	13.42	16.18
10%	0-5mm	2.49	2.52	1.69	1.65	15.83	21.94
	5-15mm	2.47	2.47	1.70	1.71	13.24	16.09
	15-25mm	2.45	2.46	1.69	1.67	12.24	15.74
15%	0-5mm	2.44	2.45	1.71	1.69	11.94	13.46
	5-15mm	2.45	2.46	1.71	1.68	9.95	12.20
	15-25mm	2.42	2.43	1.68	1.67	9.89	12.13
20%	0-5mm	2.50	2.53	1.71	1.66	20.67	23.68
	5-15mm	2.46	2.47	1.70	1.69	18.58	19.43
	15-25mm	247	2.49	1.70	1.68	18.21	20.67
25%	0-5mm	2.50	2.52	1.75	1.66	19.46	24.64
	5-15mm	2.46	2.48	1.71	1.68	18.62	20.47
	15-25mm	2.45	2.46	1.70	1.68	18.23	19.22
Marking:							
I – ceramic drying at presence of sodium sulphate, II –ceramic after salt extraction							

In the tested ceramic from the face wall layer, a high share of porosity responsible for capillary flow was found. In case of drying in presence of salts, the share of pores from this range increases while simultaneously decreasing total open porosity. After salt extraction for concentration to 15%, there is a visible share increase of pores>30nm with comparable values from the 3.0-30nm range. It is the effect of salt crystallization. Researches by Koniorczyk et al. [10] indicate that in case of a brick wall the tensions at surface can reach values close to brick tensile strength about 1MPa. This can lead to the appearance of scratches and surface damages of the wall. Above this concentration, the porosity results are close to the initial sample (marked in the Table 1 as „0"). It can be assumed that it is the limit value by which the subflorescence process starts.

Table 2. Results of surface layer porosity test (0-5mm)

Concentration of Na_2SO_4	Open porosity %	Pore range share, %		
		>30nm	3.0-30nm	<3nm
0% (initial)	32.4	1.7	10.8	19.9
Ceramic drying at presence of salt				
5%	31.9	3.7	11.3	16.9
10%	32.2	2.4	13.0	16.8
15%	30.1	2.5	12.9	14.6
20%	31.2	2.2	10.5	18.4
25%	29.9	2.0	11.9	15.9
Ceramic after salt extraction				
5%	31.9	4.1	10.0	19.2
10%	34.5	5.6	10.7	18.1
15%	35.0	5.3	12.4	17.3
20%	31.2	2.0	10.0	18.2
25%	31.0	2.8	11.0	17.3

The observation of samples made by a confocal microscope in which salt crystallization occurred showed that the total destruction of ceramic caused by sulphates concerns a layer that was 407μm thick (Figure 7). The observed damages of salted ceramic can be compared to rock weathering by salt –defined as a kind of physical weathering consisted in crumbling of material through a physical activity of salt. Salt weathering occurs when it crystallizes in pores and cracks of ceramic.

Figure 7. Picture of damage on ceramic surface resulting from sodium sulphate crystallization based on confocal microscopy

A crystal of salt exerts increasing pressure on pore walls causing a breakup of ceramic material. This breakup can be both granular (often defined as "wall powdering"), as well as block breakup causing structural damage. In case of sodium sulphate, it is a granular breakup.

4. Conclusion

In this paper, the test results of salt crystallization in traditional ceramic were presented. The tests were aimed at definition of the material destruction range with sodium crystallization and the limit concentration at which the intensive subflorescence process initiates. Solutions with concentrations of 5, 10, 15, 20 and 25%were used. It was found that up to concentration of 15%, the crystallizing salt decreased the specific weight of the samples. Within the range of these concentrations, the salt extraction is possible by soaking – the material has a volume density close to the sample where salt did not crystallize. At higher concentrations, there is an accumulation of salt under the surface which destroys the ceramic. One of the destruction evaluation methods is a confocal microscopy which enables 3D surface depiction. It also allows identifying the destruction mechanism.

Acknowledgment

References

[1]   A.E. Grimmer, "A Glossary of Historic Masonry Deterioration Problems and Preservation Treatments", *Department of Interior National Park Service, Preservation Assistance Division* Washington1984.
[2]   M. London, "How to Care for Old and Historic Brick and Stone", Preservation Press Washington 1988.
[3]   F.M. Hueston, "Subflorescence: the deterioration of historic stone &masonry through the crystallization of water-soluble salts" *The National Training Centre for Stone & Masonry Trades* Longwood 1996.
[4]   M. Rokiel, "Waterproofing in construction – guide". Dom Wydawniczy Medium Warsaw 2006, (in Polish).
[5]   L. Pel, H. Huinink, K. Kopinga, R.P.J. van Hees, O.C.G. Adan, "Efflorescence pathway diagram: understanding salt weathering". Constr. Build.Mater.18(5) 2004, pp 309-313.
[6]   ASTM D4404 - 10 "Standard Test Method for Determination of Pore Volume and Pore Volume Distribution of Soil and Rock by Mercury Intrusion Porosimetry".
[7]   IUPAC Reporting Physic sorption Data, Pure Appl. Chem., 57 (1985) 603J.
[8]   M. Wesołowska, "Impact of the external electromagnetic field on the kinetics ofmoistening and drying process in ceramic composite". Doctoral dissertation. Lodz University of Technology 2000. (in Polish)
[9]   Z. Tokarski, S. Wolfke, "Corrosion of ceramic building materials.Arkady, Warsaw 1969. (in Polish)
[10]   M. Koniorczyk, W. Grymin, P. Konca, D. Gawin, "Salt transport and crystalization in building materials during drying", *Folia Scientiarum Universitatis Technicae Resoviensis*z. 59, nr 3/III, pp 25-32 (in Polish).