Microscopic study of weathering of white Flemish stone from the monumental Church of Our Lady in Breda, The Netherlands

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This paper deals with the use of an integrated microscopic method to assist in the investigation of the causes and the extent of decay of the stones and ornaments in the gothic *Church of Our Lady* in Breda, The Netherlands. The purpose of the study was to determine whether conservation measures were necessa-ry. As part of the investigation 8 fluorescent thin sections were prepared from cores removed from the Flemish sandy limestone, used to build parts of the church and 4 from cores of an oolitic limestone, used for some of the architectonic ornaments and examined by means of fluorescent microscopy. The results showed that the processes and extent of decay vary for the two types of stone, although the causes of decay were similar. In the case of the sandy limestone, the decay processes, mainly conversion of calcite to gypsum and the formation of black crusts, were found to be largely restricted to the fine-grained calcite matrix. With regard to the oolitic limestone, the processes of decay were found not only to be confined to the microcrystalline calcite matrix, but also to the calciticoolites. In both cases, however, the occurrence, distribution and interconnectivity of cracks and micropores seemed to play an important role in the decay processes. In general, the stones that had always been exposed to outdoor weather were found to be more severely decayed than those in sheltered areas.

Key words: Natural stone, white Flemish stone, Gobertange, Lede, conservation, microscopic investigation

1 Introduction

1.1 General

In April 1991, a cooperation project concerning the conservation of the Church of Our Lady in Breda was initiated. A committee comprising specialists on monuments from TNO Building and Construction Research, the Technical Univer-sity of Delft, Architect Bureau van Stigt, the Government Building Agency and the Nether-lands Government Service for the Preservation of Monuments and Historic Buildings was formed and charged with the responsibility of planning a durable conservation policy for this monument.

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1.2 The monument

The gothic Church of Our Lady is located in Breda, an urban area in North Brabant. The oldest part of the church dates back to the XV Century, but the construction work was mainly carried out in the XVI Century. The surface of the walls is made of limestone blocks of Gobertange and Lede stone (Nijs 1985). The architectonic ornaments of the church are made of various types of limestone (Fig. 1).

During the last and the present centuries, three restoration campaigns have taken place. These restorations involved the tower (1843-1875 and 1950), the choir and the transept (1902-1939). During the restoration campaign around 1925, the walls of the upper portion of the transept were partly sheltered from outdoor exposure under a roof. The extent of decay of these sheltered blocks of limestone could be compared with that of the same type of stone that had been exposed since the XVI Century. This way a contribution could be made to the study concerning the influence of environmental pollution on the decay of stone monuments.

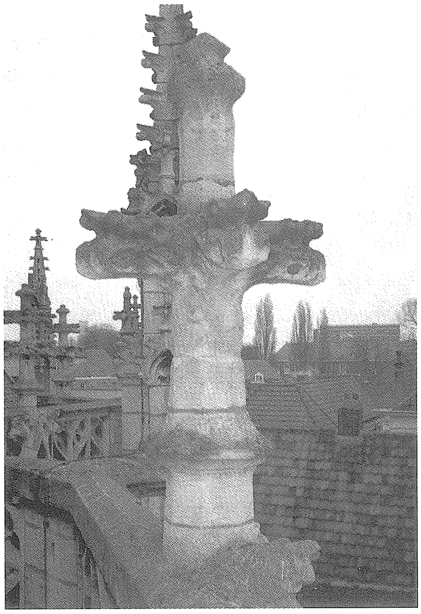


Fig. 1. Overview of some of the architechtonic ornaments of the monument.

1.3 Damage and possible causes

The main types of damage of the walls and the architectonic ornaments observed in a preliminary visual inspection were the following:

- black crusts, formed especially on stone surfaces that are not exposed to rain wash-out (Fig. 2);
- erosion of stone surfaces exposed to rain wash-out (Fig. 3);
- delamination of the surface of the stone, due to wrong mortars used in the repairs;
- "hard" pointing and biodeterioration, which tend to occur on the stone surfaces that remain wet for most part of the year.

In addition, some of the stone blocks were found to show loss of material in variable amounts (Figs. 2 and 3). In some cases the edges or corners of stones were found to have become round. From the results of the preliminary diagnosis, it was found that the decay of the stone in the black crust zone was mainly due to conversion of the calcite to gypsum referred to as sulphation. This process of decay is believed to result from attack of the sulphur in the atmosphere, which appears to be connected with the exposure of the stones to the environmental elements such as wind, rain and sunshine (Bernardi et al. 1985, Schiavon 1992, Schiavon et al. 1999).

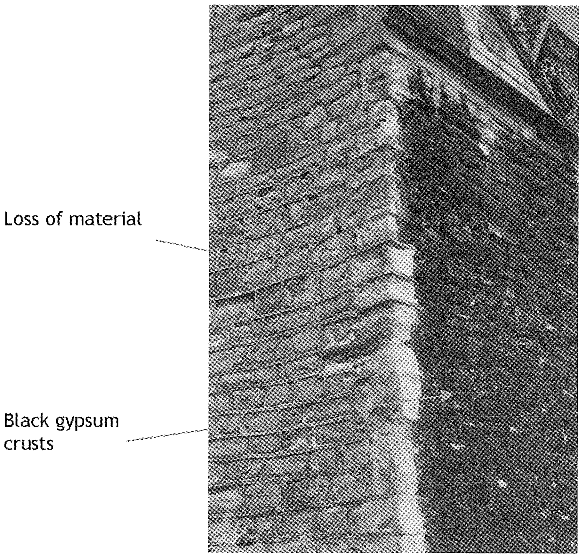


Fig. 2. Overview of portion of a wall constructed with the sandy limestone showing two forms of deterioration: material loss and formation of black gypsum crusts.

1.4 Previous microscopic study

During the first phase of this project, it became obvious that more knowledge of the deterioration processes and the extent of the decay of the sandy limestones used to build parts of the church was crucial in determining whether conservation measures were necessary. For this reason, a number of investigations was carried out in order to determine the essential material properties of the stone with regard to these decay mechanisms. Insitu measurements to obtain certain information about the stone, such as hardness profile and water absorption were performed. In the laboratory, porosity and sulphate analyses as well as scanning electron microscopic (SEM) investigations were carried out. The results showed that the stone that had been used for the walls was, in general, of sound quality. Only the most external surface (a few millimeters thick, including the crust) showed some loss of cohesion. In the first circa 2 mm, the sulphate content was found to be significantly higher than deeper in the stone. Although these results were important, they could not be used to characterize the microstructure of the stone and to study the actual processes of deterioration and to determine the extent of the decay of these stones. It was also not possible to find evidence of further decay of the sound portion of the stone, and to predict the rate of development of future deterioration processes.

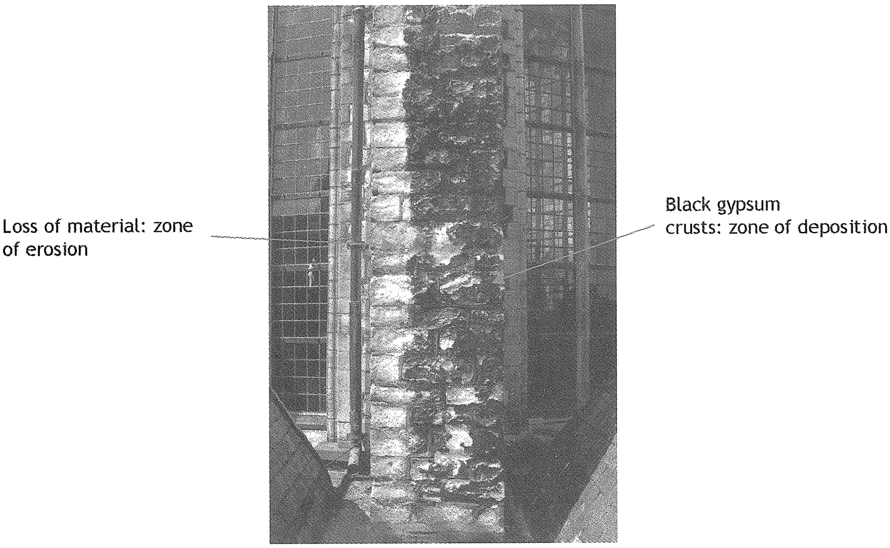


Fig. 3. A supporting pillar constructed with the sandy limestone at the south-western part of the church showing material loss from erosion (left) and dry-deposition (right) – leading to the formation of black gypsum crusts.

Because of lack of adequate information about the microstructure, one could not determine the processes by which the sulphate penetrated the stone. Neither was it possible to determine the origin of the gypsum in the stone that was identified from the SEM analyses. The occurrence of gypsum in calcareous stones used in monuments and especially located in urban areas is usually used as an 'indicator' of the decay of the stone. Although this may be true, it is not in all cases that the presence of gypsum in calcareous stones results from decay processes. Gypsum can be formed in such stones as a result of the following:

- conversion of the calcite matrix in the stone to gypsum;
- recrystallization of gypsum already existing in the stone from previous decay processes;
- dissolution of particles of gypsum from the atmosphere that are deposited on the surface of the stone which later crystallize in the stone;
- or perhaps from combinations of these three possibilities.

In addition, a preliminary optical microscopic study, coupled with image analysis was carried out on 3 samples of a sandy limestone in order to obtain a first hand information about the extent of dacay of the stone. Only the preliminary PFM analysis enabled a picture to be formed of the decay processes occurring in the stone. It made it possible to characterise the internal structure of the samples of the sandy limestone (including microporosity distribution), to determine the processes of decay and to delineate the extent of decay in the stones. This set of information was of fundamental importance in the assessing the severity of decay, of the stones in view of the conservation policy that was to be planned. Although some basic information related to the decay processes was gathered from the PFM investigation, the results were limited in that only a few samples from one part of the church were used for the study.

This paper deals with the second phase of the PFM investigation. It reports the results of a detailed thin section analysis of 8 samples of the sandy limestone and 4 samples of an oolitic limestone used for some of the architectonic ornaments. The purpose of this study was to gather adequate information with regard to the processes and the extent of decay of the stones and ornaments so that together with other investigations concerning this project, a suitable conservation policy could be planned for this monument.

2 Sampling

Sampling was carried out in areas representative of the forms of decay mentioned (see Section 1.3). Some relevant information regarding the samples have been summarised in Table 1.

Table 1. Summary of the relevant information concerning the samples examined

Sample code	Type of stone	Type of stone
T-ZO-1-Bi	Sandy limestone (Gobertange or Lede)	South-east: sheltered area
T-ZO-2-Bi	Same	Same
T-ZO-2-Bu	Same	South-east: unsheltered area
T-ZO-3-Bu	Same	Same
T-ZW-2-Bi	Same	South-west: sheltered area
T-ZW-3-Bi	Same	Same
T-ZW-3-Bu	Same	South-west: unsheltered area
T-ZW-4-Bu	Same	Same
Nr. 10.1	Oolitic limestone	Unsheltered
Nr. 11.1	Same	Same
Nr. 12.1 a	Same	Same
Nr. 12.1 b	Same	Same

3 Microscopic analysis

An integrated system of polarising and fluorescent microscopy (PFM) was used to characterise the mineralogy and internal structure of the samples. Prior to this, at least one thin section was prepared from each of the samples. The thin sections were prepared by first sawing small specimens measuring about 50 mm x 30 mm x 15 mm from relevant portions of the samples. Where necessary the specimens were removed in such a manner that they included the exposed surface layers. After initial drying at room temperature, followed by vacuumimpregnation with an epoxy resin containing a fluorescent dye, the specimens were glued to an object glass, cut and finally ground to a thickness of 25-30 μm. The epoxy-impregnation served two purposes: it was used to stabilize the material and to ensure that all the voids in the specimens were completely filled with the resin. This is quite essential because it helps to reveal features of the microstructure and texture. Information obtained included the mineralogical composition and internal structure of the stones, such as the pattern of cracking, the presence of newly formed reaction products and any changes in the material as a result of the formation of these new products. Evaluation of these aspects usually provides clues for reliably establishing the causes and mechanisms of deterioration of the materials.

4 Results

4.1 Specimen composition and characteristics

The limestone blocks of Gobertange and Lede stone were composed of fine-grained limestone, rich in quartz, with a few percent of glauconite, oxides and some remnants of fossils (Fig. 4). From the surface, the stone consisted of outermost black crust (Fig. 5), followed by a decay zone and deeper further, the intact or sound zone. The architechtonic ornaments were composed of oolitic limestone (oomicrite), dispersed in a matrix of calcite. The ooids consisted of foraminifera that were filled with calcite (Fig. 5). Just as in the case of the sandy limestone, the crust here was well-developed (Fig. 6), regardless of the fact that the samples were removed from unsheltered areas. The composition, internal structure and other characteristics of the samples, as well as the extent of decay have been summarised in Tables 2 and 3.

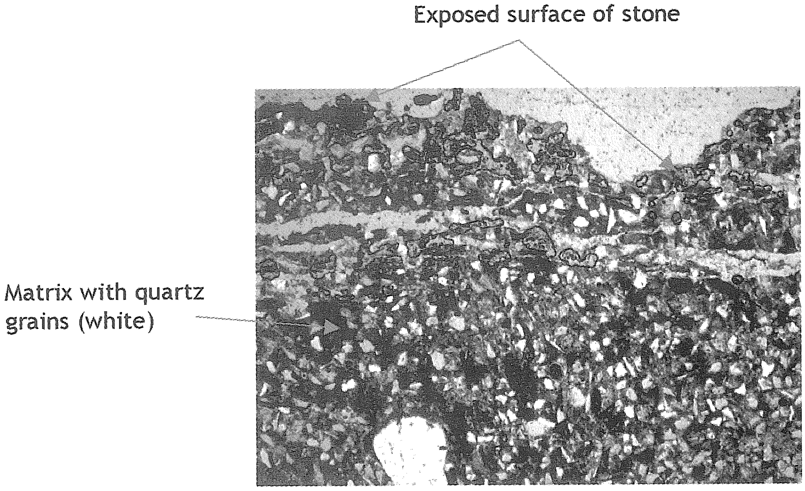


Fig. 4. PFM-micrograph of a sample of the sandy limestone (unsheltered) showing an overview of the stone from the exposed surface, the crust with gypsum layer and portion of the sound stone. Size of micrograph is 5.4 mm x 3.5 mm.

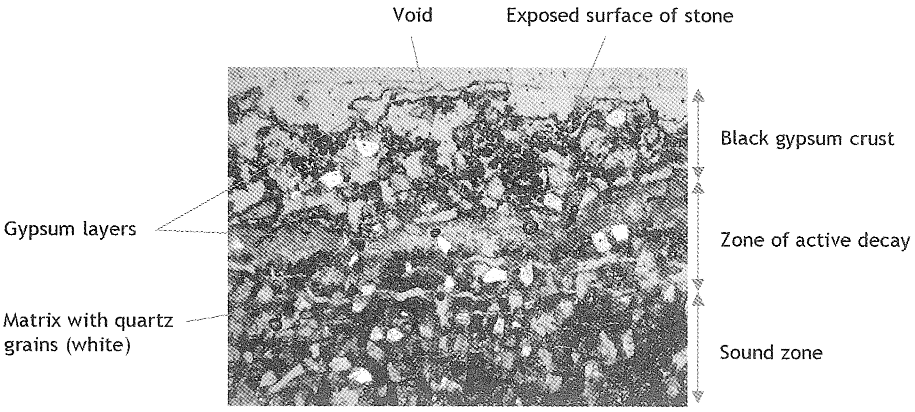
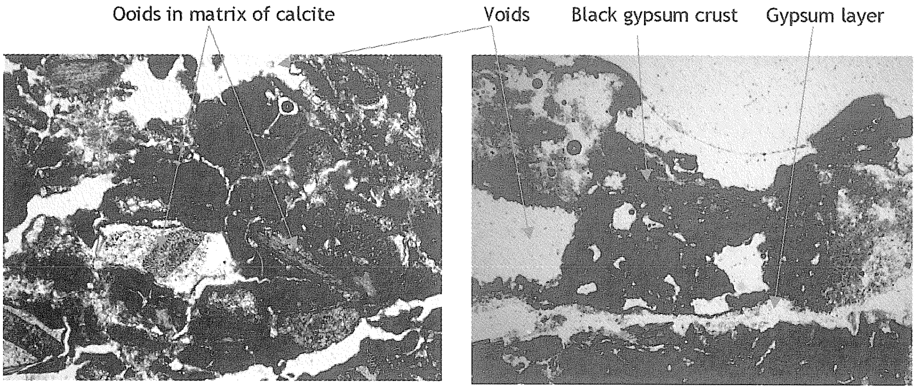


Fig. 5. PFM-micrograph of a sample of the sandy limestone (unsheltered) showing details of various zones of the stone: from the black crust with gypsum layers, the decay zone and part of the sound stone. Size of micrograph is 2.7 mm x 1.8 mm.



a = sound zone of stone

b = surface zone of stone

Fig. 6. PFM-micrograph of a sample of the oolitic limestone (ornament: unsheltered) showing overview of sound stone and details of the surface zone. Size of micrograph is 2.7 mm x 1.8 mm.

Table 2. Summary of the results of the microscopic analysis of samples of the sandy limestone

Sample code	Mineralogical composition	Extent of crust (μm)	Depth of decay (decay zone)
T-ZO-1-Bi	fine-grained limestone, rich in quartz (10-20 % by volume) with a few percent of glauconite, oxides some fossils	0 - 450	up to circa 250 μm from from the surface of the sample
T-ZO-2-Bi	same as for sample T-ZO-1-Bi	0 - 150	up to circa 150 mm from the sample surface
T-ZO-2-Bu	same as for sample T-ZO-1-Bi; a number of cracks parallel to the surface of sample	300 - 800	up to circa 4 mm
T-ZO-3-Bu	same as for sample T-ZO-2-Bu	300 - 500	up to circa 1.2 mm
T-ZW-2-Bi	same as for sample T-ZO-2-Bu	0 - 500	1 to 1.5 mm
T-ZW-3-Bi	same as for sample T-ZO-2-Bu	absent	no evidence of decay
T-ZW-3-Bu	same as for sample T-ZO-2-Bu	< 200	up to circa 3 mm
T-ZW-4-Bu	same as for sample T-ZO-2-Bu	150 - 200	up to circa 3 mm

Table 3. Summary of the results of the microscopic analysis of samples of the ornaments

Sample code	Mineralogical composition	Extent of crust (μm)	Depth of decay (decay zone)
Nr. 10.1	oolitic limestone (oomicrite); de ooids consist of foraminifera that are filled with calcite	circa 50 mm	up to circa 50 μm (0.05 mm)
Nr. 11.1	same as for sample Nr. 10.1	absent	up to circa 50 mm
Nr. 12.1a	same as for sample Nr. 10.1	2.5 - 3 mm	the whole specimen in the thin section (≥ 50 mm)
Nr. 12.1b	same as for sample Nr. 10.1	2 - 2.5 mm	the whole specimen in the thin section (≥ 50 mm)

4.2 Pattern of decay

Analysis of the fluorescent thin sections revealed that the pattern (or processes) of decay and its vary for the two types of limestone investigated, although the causes of decay are the same. For the sandy limestone, the decay processes (dissolution and conversion of calcite to gypsum - the so-called sulphation processes), formation of black crusts, loss of cohesion and material loss were found to be largely restricted to the finegrained calcite matrix, leaving the quartz and glauconite grains, as well as the remnants of fossils unattacked. In the crusts, these quartz grains were found in some cases, detached from the matrix, which appeared leached (Fig. 7). - Primary (newly formed) and recrystallized gypsum were common in existing voids and cracks in the zone of attack (Fig. 8).

With respect to the oomicrite, the processes of decay were found not only to be confined to the microcrystalline calcite matrix but also to the calciticoolites (Fig. 9). The intensity of deterioration, however, appeared to be greater with respect to the calcitic matrix than to the oolitic grains. In most cases, the oolites appeared virtually unattacked or only partially attacked. Evidence from the calcitic remnants in the central portion of the oolites suggested that the deterioration process was initiated from the outermost layer towards the center (Fig. 9a). This decay of the oolitic grains had apparently contributed to the increase in porosity of the stone. This evidence is in agreement with observations made by Bernardi et al. in 1985 and Camuffo et al. in 1999. The observations made here are, however, contrary to those made by Schiavon (1992) and Schiavon et al. (1999) on samples of oomicrite in which he found the calcitic oolites to be virtually unaffected. He found in the same study, however, that the oolites in samples of an oosparite were deteriorated in preference to the sparite cement.

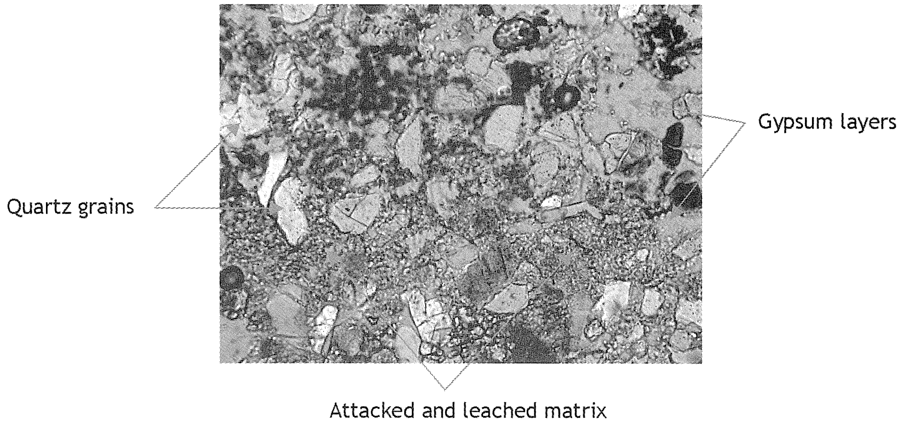


Fig. 7. PFM-micrograph of a sample of the sandy limestone (sheltered) showing the structure of the crust and the zone of active attack: the matrix appears leached leaving a 'skeleton' stone with the matrix almost detached from the quartz grains. Size of micrograph is 2.7 mm x 1.8 mm.

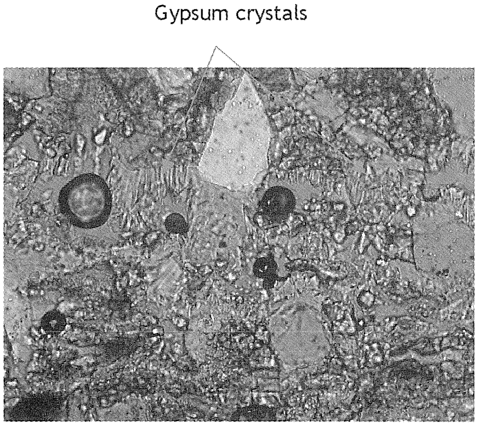


Fig. 8. PFM-micrograph of a sample of the sandy limestone (sheltered) showing gypsum crystallisation in voids and cracks. Size of micrograph is 1.4 mm x 0.9 mm.

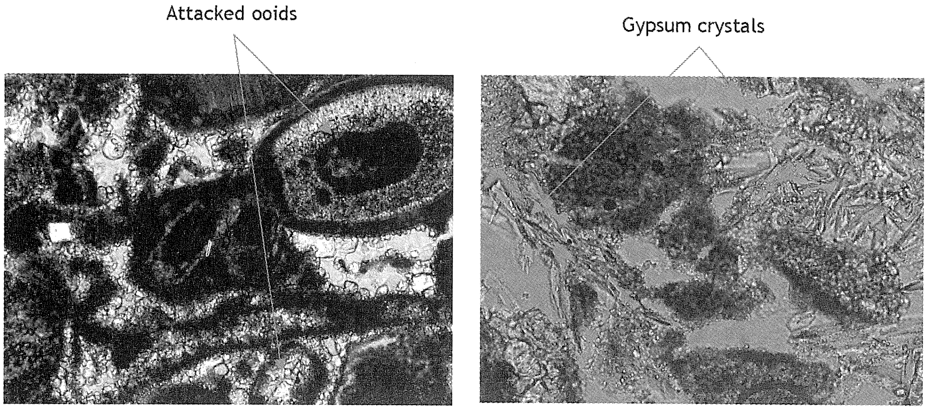
In all cases, the microstructure of the specimens from the surface into the stone showed the following features:

- A crust with variable thickness ranging from nothing (zero) up to a few hundreds of microns. This crust is, in general, composed of loosely bonded materials of gypsum (layered or in a form of finely-divided crystals), black particles (mainly soot or dirt) and partially disintegrated calcite matrix (Figs. 4, 5 and 6).
- A layer of gypsum directly under the crust, measuring a few tens of microns in thickness (Figs. 5 and 6). Finely divided crystals of gypsum co-existing with partially disintegrated calcite matrix, voids and cracks and in the case of the oomicrite, also partially disintegrated calcitic oolites. Depending on the type of stone this zone, referred to (in this study) as the decay zone, usually ranged in thickness from a few tens of microns up to a few millimeters for the sandy limestone. In the case of the oomicrites, it involved, in some cases, the whole stone (see Table 3).
- The sound portion of the stone, where there was no evidence of decay.

No coal-derived aluminosilicate or fly ash particles were identified in any of the thin sections of the samples of stones that were studied. Such particles are believed to catalyze the deterioration processes of calcareous building stones in monuments (Camuffo and Bernardi, 1990, Camuffo et al., 1999 and Moberg et al., 2000). Leysen et al. (1989) rarely found such particles also in a study on similar sandy limestone samples in a cathedral in Belgium. There was no evidence of the Ferich brown line that was identified by Leysen et al. (1989). The soot particles identified did not show any stratigraphic distribution; they were randomly distributed.

In samples of the sandy limestone as well the oomicrite the occurrence, distribution and interconnectivity of cracks and micropores seemed to play an important role in the decay processes. With regard to the oomicrites, nearly all the microcracks and micropores were found to be interconnected with each other and with the exposed surface of the specimens. This occurs not only in the decay zone but also in areas where the decay processes had not begun. The pattern of these microcracks and micropores shows that most of them were inherent and had only increased as a result of the decay processes. For all the specimens studied, the decay processes appeared to progress along the microcracks or micropores.

In most of these microcracks and micropores, large, sometimes fingerlike crystals of gypsum were observed. In addition, finely divided crystals of gypsum were also identified, often intermixed or co-existing with partially disintegrated matrix showing clear evidence of in situ dissolution and conversion of the finegrained calcite matrix to gypsum. In the areas where these features were observed the limestone matrix appeared to be 'torn' into pieces. As a consequence there is an increase in porosity of the stone in this zone (Figs. 7 and 8). Most of the large crystals of gypsum that were observed appeared to have been the result of recrystallization. Some of these large crystals seemed to have used the more resistant quartz grains and in some cases the unattacked calcite as nuclei for precipitation (Figs. 8). Also at the edge of the matrix material and along the oolites bordering these microcracks and micropores relatively large dog-toothed crystals of calcite were found (Fig. 9a). These last two features provide evidence of recrystallization of calcite and gypsum.



a = overview

b = details

Fig. 9. PFM-micrograph of a sample of the oolitic limestone (sheltered) showing the internal structure and pattern of decay of the stone: the calcitic matrix and the ooids are gradually converted to gypsum. There is also recrystallisation of gypsum in the voids. Size of micrograph is: a. 2.7 mm x 1.8 mm; b. 1.4 mm x 0.9 mm.

Schiavon (1992) and Schiavon et al. (1999) related the differences in the pattern of decay between oosparite and oomicrite to the differences in microporosity (permeability) between these two lithologic stones. According to him, current studies indicate that in oosparites the microporosity is mainly within the oolite grains. By contrast, in oomicrites most of the interconnecting pores, affecting the stone permeability, are located in the micritic cement. The interconnectivity of the microcracks and micropores observed in this study, is likely to have played a paramount role in the decay processes of the stones.

One remarkable observation made from the thin section analysis was that in 4 of the 8 thin sections of the sandy limestone samples (Gobertange and Lede stones) that were examined (T-ZO-2-Bu, T-ZO-3-Bu, T-ZW-3-Bu and T-ZW-4-Bu), cracks oriented parallel to the surface of the samples were observed (Figs. 1 and 6). Also in these specimens the processes of decay appeared to be restricted to the calcite matrix in the area between the 'parallel' cracks and the surface of the samples - referred to as the decay zone. Deeper in the stone, that is, beyond the 'parallel' cracks no evidences, such as conversion of calcite, presence of interconnected microcracks or pores, etc. were found that suggested any decay or the possibility of decay of the stone. Similar parallel cracks have also been observed by Bernardi et al. (1985) in samples of an oomicrite but their relationship to the decay zone was not made. In the zone of decay of these four specimens, the amount of stone that has been converted is relatively small. Microscopic analyses of the thin-sections, using a linear traverse technique, revealed that the amount of converted calcite to gypsum in this decay zone is approximately 3 to 12 % by volume of the stone. This extent of decay is relatively insignificant if compared to the unconverted calcite. More recrystallized gypsum was found deeper in the material than near the surface and vice-versa for the converted gypsum. From Table 1 also it is clear that the stones that had been exposed to outdoor weather showed severer forms of decay than the ones in sheltered areas since circa 1925.

5 Concluding remarks

The PFM analysis has yielded very useful information about the samples of stones investigated. It has shown clear evidence of the decay processes in the stones and areas where (active) decay is taking place. It has enabled accurate determination of the extent of decay of the stone samples. In addition, the microstructural characteristics of the stone that influence the decay processes such as the interconnectivity of microcracks and micropores have also been identified.

From the investigation, a distinction has been made between the distribution and forms of gypsum that occur in the stone which could not be distinguished from the SEM analysis in the first phase of this project. This distinction enabled for example, estimation of the amount of decayed material in the sandy limestone samples. This set of information about the building stones and the ornaments, which from previous preliminary investigations could not be obtained, has been found to be very useful in the planning of a suitable conservation policy for this monument - the Church of Our Lady in Breda, The Netherlands. The Gobertange and Lede stone has been found not to be in structural danger with regard to decay. With regard to the ornaments, the extent of decay is substantial.

6 References

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