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# THE INFLUENCE OF ACID RAINS ON THE LITHOTHAMNIAN LIMESTONE ON THE GALLERY OF THE MARY'S ASCENSION CATHEDRAL, ZAGREB, CROATIA

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**Key-words:** Damages of limestone, Cathedral of Zagreb, Pollution, Acid rain

Urban, environmental pollution, caused by acid rains and damages of stone elements on Cathedral of Zagreb are described. On the surfaces of limestone elements that are in the »shade«, the black scabs have developed. The outher crusts, and inner powdery matter of the black scabs have been investigated by microscopy, and analyzed by means of x-ray. thermal and chemical analyses. They contain gypsum, calcite, soot, and sporadic fly ash.

**Ključne riječi:** Oštećenja vapnenca, Zagrebačka katedrala, Zagađenje, Kisele kiše

Opisani su zagađenje urbanog okoliša, sastojci kisele kiše i oštećenja kamenih elemenata galerije zagrebačke katedrale. Na površini vapnenačkih elemenata koji su u »sjeni« nastale su crne kraste. Vanjske kore i unutarnja praškasta tvar crnih krasta analizirane su mikroskopski, rendgenski, termički i kemijski. Sadže gips, kalcit, čađu i ponekad lebdeći pepeo.

## Introduction

The cathedral of Mary's Ascension in Zagreb was built in its present neogothic style between 1880 and 1902, according to a desing by F. Schmidt and H. Bolle. It was rebuilt after a devastating earthquake which struck Zagreb in 1880.

The cathedral was rebuilt with stone from demolished old cathedral and with lithothamnian limestone from the quarries in Bizek and the Vrapče Potok, places on the western slopes of the Medvednica Mt., and with vinicite, a porous and soft limestone from Vinica near Varaždin.

The cathedral was renovated in the 30eis and late 60ies. The latest renovation began in 1993. The first gallery with two console cornices and a balustrade with phials is to be repaired in the first phase.

Damages of the lithothamnian limestone of the cathedral were thoroughly examined by Marić (1938). He analyzed the stone surface by microscopic and chemical methods. The microscopic analyses of the vegetation (made by Mr. Pevalek) on the stone surface gave the following results:

- undeveloped fungus mycelia without greater significance were found, along wiht a few short rod-shaped algae of the genus Stichococcus,
- on the stone surface and on the walls of the cavities near the surface there was green algae — a community of protopleurococcoid forms,
- members of the genus Pleurococcus and the genus Aptoccus were found on the stone surface and adjoining it, and
- real endolites were not found.

The above findings show that whether in or on the inbuilt lithothamnian limestone there are not any real endolites, a vegetation that could by its life functions damaged the stone.

It was determined by mineralogical, petrographic and chemical investigations that the primary cause of surface erosion of the lithothamnian limestone is the transformation of calcite to gypsum under the influence of the sulphuric acid in rain. The analyzed samples of the lithothamnian limestone from the quarries, where the stone for the cathedral was exploited, do not contain gypsum nor other sulphuric and/or sulphatic minerals. It was established that the samples of damaged stone from the cathedral contained from 7.70% to 23.74% gypsum.

## Atmospheric pollution of urban environment

Having established the causes of damage in lithohamnion limestone of the cathedral Marić (1938) gave an account of the data concerning atmosphere pollution in Zagreb during the 30ies. From the data collected for the period between May 28th to December 14th 1936, the quantity of ion $SO_4^{--}$ was about 3 mg/l or 3 g/m$^3$ in rain, according to the measurements taken by the Hydrometeorogical Institute in Zagreb. At that time households, factories and steam engines in Zagreb annually burnt approximately 200,000 tons of coal containing on the average some 2.25% of combustible sulphur. Calculations showed that the atmosphere in Zagreb and its surroundings received some 1,380 wagons (10 tons each) of concetrated sulphuric acid.

An example of urban environment pollution at that time are data given by Kieslinger (1932). In relation to the amount of coal annually burnt in Vienna, the air was polluted up to 10,000 wagons of sulphuric acid and 13,000 wagons of soot. In Linz the sulphuric acid amounted to 138 wagons and in Innsbruck to 114 wagons.

From the point of view of air pollution with sulphur dioxide some interesting information about the greatest »producers« of $SO_2$ was provided by Feilden (1988, Table 1).

Table 1 Largest producers of $SO_2$ in Europe (1982) (After: Feilden, 1988)

| Country | Pollution produced (million tonnes) 1982 | Pollution transmitted to another country | Change 1972—82 | $SO_2$ weight (kg) per person (1982) |
|---|---|---|---|---|
| USSR | 25.5 | −2.05 | + 9% | 211 |
| United Kingdom | 4.25 | +2.31 | − 24% | 168 |
| East Germany | 4.0 | +2.28 | 0 | 527 |
| West Germany | 3.51 | +1.4 | − 10% | 126 |
| Czehoslovakia | 3.37 | +0.36 | + 16% | 485 |
| Italy | 3.07 | +1.08 | − 3% | 119 |
| France | 2.89 | +0.32 | − 10% | 119 |
| Poland | 2.5 | −0.32 | − 17% | 155 |
| Spain | 2.09 | +0.49 | + 61% | — |
| Rumania | 2.0 | +0.01 | +235% | 197 |

In Zagreb atmosphere pollution is measured by Center for Meteorological Research of the Hydrometeorological Institute of the Republic of Croatia at Grič, at the measuring station on the Medvednica Mt. (at Puntijarka), and occasionally at the Cathedral fo Zagreb.

According to Lisac (1989) the annual mean values of the degree of acidity expressed as a concentration of hydrogen ions between 1970 and 1986 are as represented in Fig. 1. The relative frequency means of pH values of precipitation at the measuring station Grič during the periods 1969—1978 and 1979—1985 can be seen in Fig. 2.

Noticeably higher degrees of acidity can be observed in precipitation between 1983 and 1986. Another significant increase from 2% to 7.5% of precipitation with pH=4 can be noticed during the second decade investigated.

According to the data from the Hydrometeorological Institute (HIRC) the monthly means of $SO_2$ and $SO_4^{--}$ concentrations at the measuring station Grič for the period 1987—1993 are presented in Figs. 3 and 4. The monthly means of

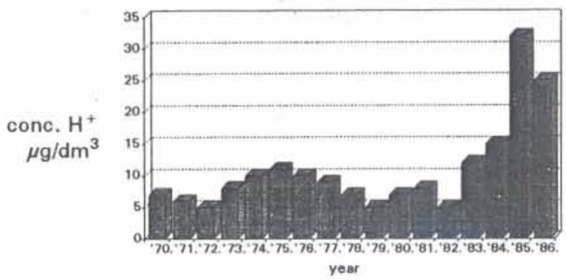


Fig. 1. The annual mean values of the degree of acidity expressed as concentration of hydrogen ions (After: Lisac, 1989)

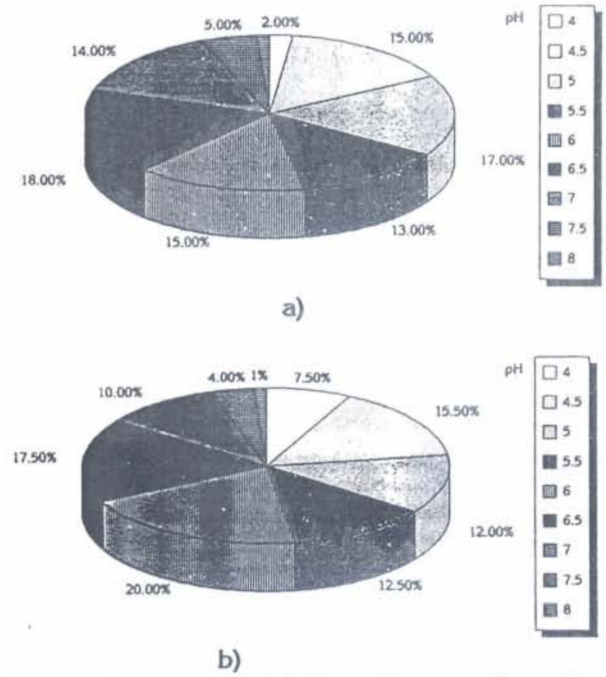


Fig. 2. pH values of precipitation at the meassuring station Grič in Zagreb (After: Lisac, 1989)
a) period 1969—1978
b) period 1979—1985

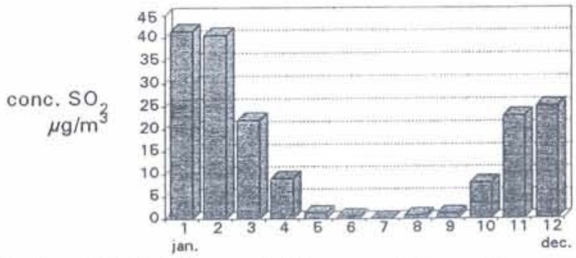


Fig. 3. Monthly means of $SO_2$ concentration at the measuring station Grič for the period 1987—1993 (Hydrometeorological Institute, Zagreb)

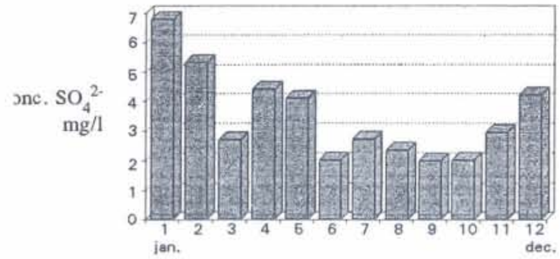


*Fig. 4. Monthly means of $SO_4^{--}$ concentration at the measuring station Grič for the period 1987—1993 (Hydrometeorological Institute, Zagreb)*

$SO_2$ concentration and of smoke at the measuring station of the Zagreb Cathedral (at Kaptol) for the period 1977—1988 are shown in Figs. 5 and 6.

It can be seen that the critical months for pollution of the atmosphere with $SO_2$ and smoke at the measuring station of the Cathedral and at Grič are from November to March. From what has been said above it follows that the Zagreb Cathedral has an environment which is considerably polluted by $SO_2$ at least five months of the year. Such pollution must influence the durability of the inbuilt limestone and have an effect on its decay.

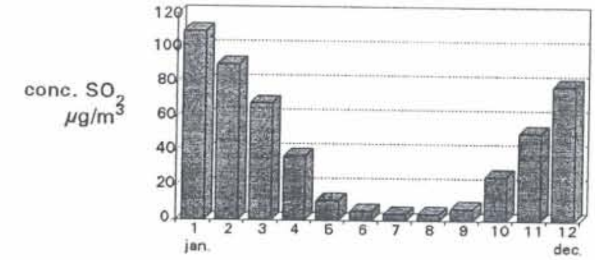


Fig. 5. Monthly means of $SO_2$ concentration at the measuring station of the Zaggreb Cathedral for the period 1977—1988 (Hydrometeorological Institute, Zagreb)

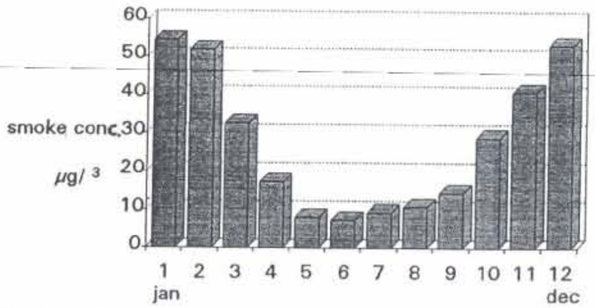


Fig. 6. Monthly means of smoke concentration at the measuring station of the Zagreb Cathedral for the period 1977—1988 (Hydrometeorological Institute, Zagreb)

Fig. 7. Surface of stone elements of the lower console cornice with black scabs getting detached from the surface of the limestone
(Photo: D. Jovičić, 1993).

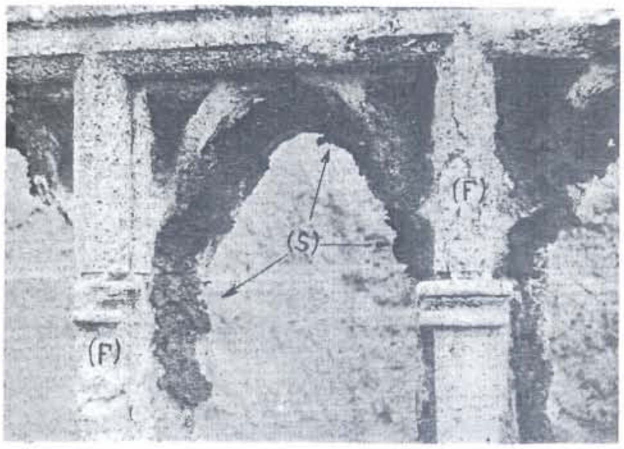


Fig. 8. Stone elements of balustrade with surface exposed to rain, cracked and flaked (F), and the parts in »shade« with black scabs (S)
(Photo: D. Jovičić, 1993)

A review of data concerning pollutants of the atmosphere in urban environments by transformations of various states of aggressive gasses and their threat for stone has been provided systematically and in detail by Winkler (1973), Amoroso and Fassina (1983), and Lazzarini and Tabasso (1986).

### Forms of corrosion of the inbuilt stone

The lithothamnian limestone built into the gallery comes from two quarries. The stone elements of the lower console cornice are built of silty lithothamnian limestone from the quarry in Vrapče Potok. The stone elements of the balustrade were made largely of the lithothamnian limestone from the quarry in Bizek, and to a minor extent from silty limestone quarried in Vrapče Potok. The silty lithothamnian limestone from the quarry in Vrapče Potok is of markedly poorer quality and resistance than the stone from the quarry in Bizek. The stone elements made from it are therefore corroded to a much greater extent.

There are two main forms of corrosion visible in the stone elements, depending on whether their surfaces are exposed to rain or they are sheltered in the »shade« (Figs. 7 and 8). Parts of the inbuilt stone which is exposed to rain are whitish and greyish, cracked and noticeably pulverized and flaked, with larger irregular pieces of stone breaking off. The parts in the »shade« are covered by black scabs.

There are three kinds of black scabs (Fig. 9):

a) black scabs firmly cleaving to the surface of the limestone, regularly occuring on stone of good physical and mechanical properties, porous, but compact between the pores;
b) black scabs getting detached from the surface of the limestone, with a whitish powder between them and the stone;
c) black scabs getting detached from the surface of the limestone in the form of irregular pieces and patches with a black crust on both sides; between the crusts there is a whitish to greyish powder; such scabs are up to several centimetres thick and they are always becoming detached from the surface of the silty lithothamnian limestone; they are found on the surface of stone elements of the lower colonnade and on parts of the balustrade.

### Composition of the black scabs

The composition of the black scabs, the outher crusts and the inner powdery matter, has been determined by microscopy, and analyzed by means of x-ray, thermal and chemical analyses.

It has been established by microscopic analysis that the black crust and the powdery matter, with

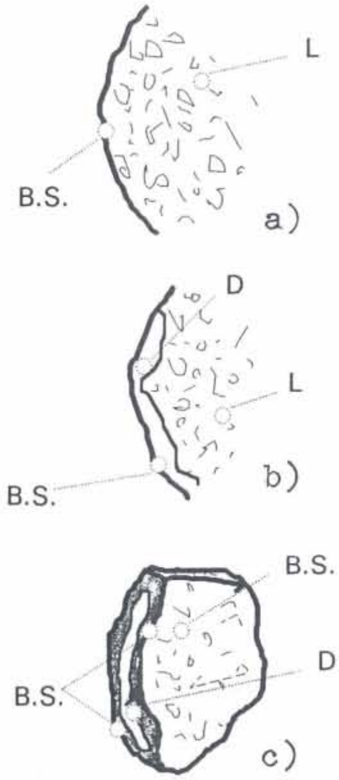


Fig. 9. Kinds of black scabs:
a) firmly cleaving to the surface of the limestone
b) getting detached from the surface of the limestone
c) getting detached like irregular pieces and patches
L limestone
BS black scab
D powdery matter

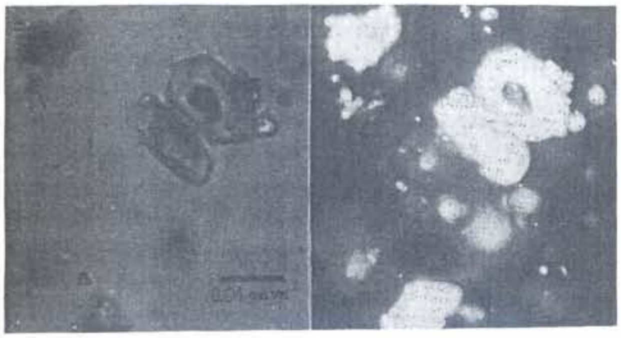

Fig. 11. Thin-section photomicrograph of the tiny idiomorphycally crystals of gypsum from the powdery matter between the crusts of the black scab (one and crossed Nicols)

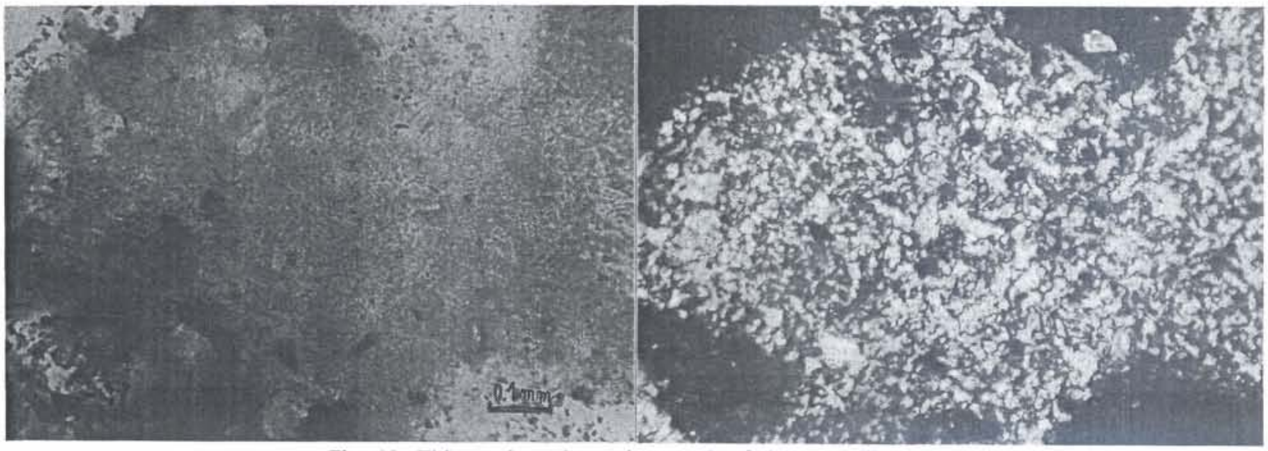


Fig. 10. Thin-section photomicrograph of the crystalline aggregate of gypsum, tiny crystals of gypsum have irregular forms, and they intertwine (one and crossed Nicols)

fragments of limestone and dirt, predominantly soot, is largely composed of gypsum.

The crusts of the detached flakes are mostly crystalline aggregate of gypsum. The tiny crystals of gypsum in this aggregate have irregular forms and they intertwine. Only sporadically can there be noticed idiomorphically criystallized gypsum (Fig. 10). Idiomorphically crystallized tiny crystals of gypsum are numerous in the powdery matter between the firm crusts of the black scabs (Fig. 11). Aggregates of thin plated crystals of gypsum when represented by electron microscopy resemble druses of gypsum, known as desert roses (Fig. 12). The black crusts with opaque soot particles contain glassy globules of fly ash (Fig. 13).

Samples of crusts and the powdery matter from the cornice of the gallery and balustrade were x-rayed (powder analysis) as well as the insoluble residues of them.

All samples of black scabs that were analyzed have an identical mineral composition. They contain gypsum, calcite, and quartz (Fig. 14 and 15).

The insoluble residues of crusts and powdery matter of the black scabs contain quartz, micaceous minerals and plagioclases (Fig. 16).

The x-rayed conditions were: voltage 34 kV, electric intensity 18 mA, sensitivity $4.10^2$, time constant 4 s, metre velocity $1^0$/min, tape velocity 10 mm/min.

Symbols for the minerals on the diffractograms are as the follows:

Gy gypsum
Cc calcite
Q quartz
T micaceous minerals
Pl plagioclases

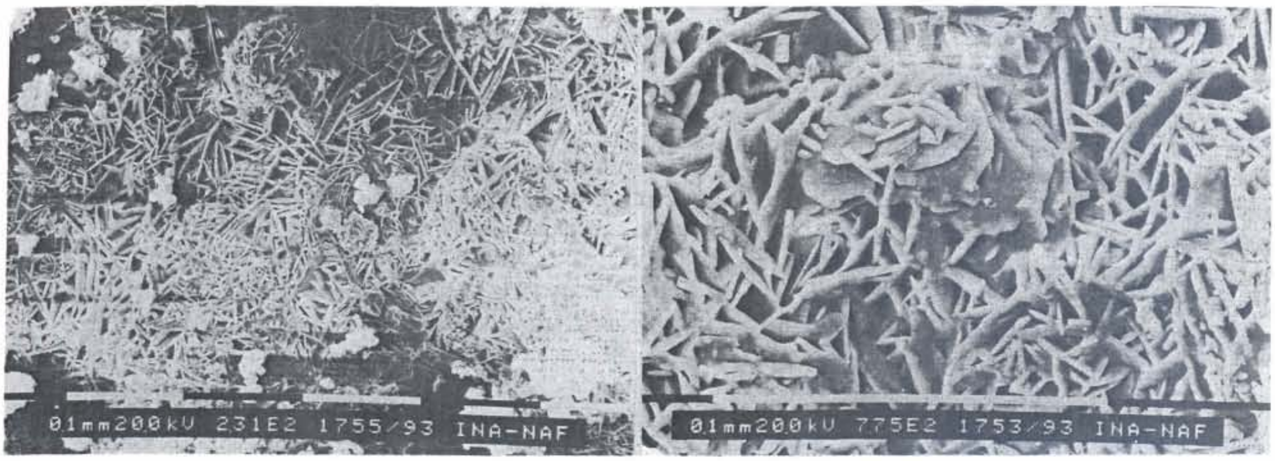


Fig. 12. Electron photomicrography of gypsum aggregate from black scab (Reproduced by kind permission of Mr. V. Labudović and INA-Naftaplin, Zagreb)

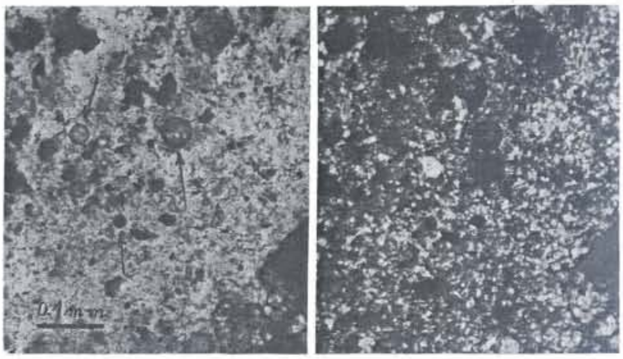

Fig. 13. Thin-section microphotographs of glassy globules of the fly ash, marked with arrows (one and crossed Nicols)

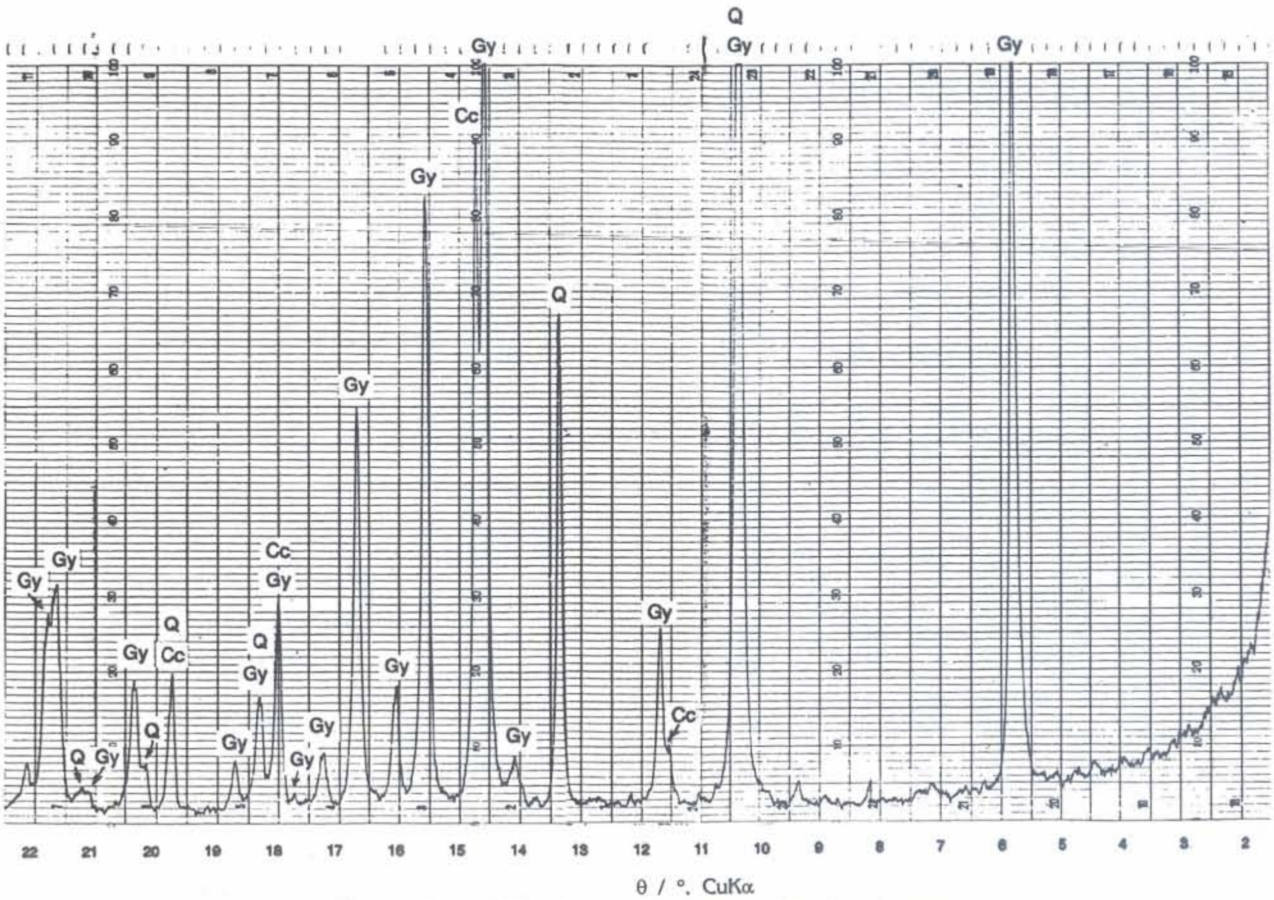


Fig. 14. X-ray diffraction powder patterns of black scab crust

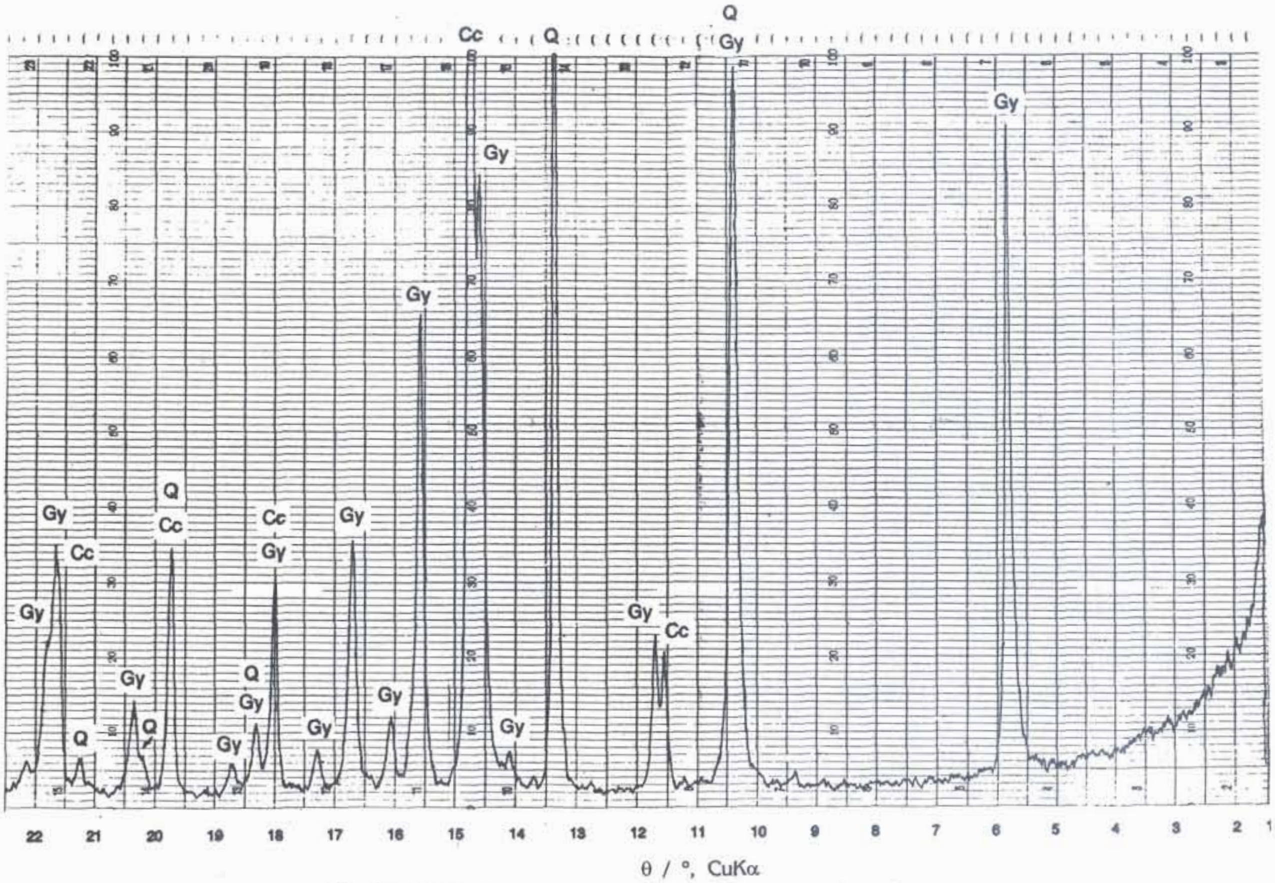


Fig. 15. X-ray diffraction powder patterns of black scab powdery matter

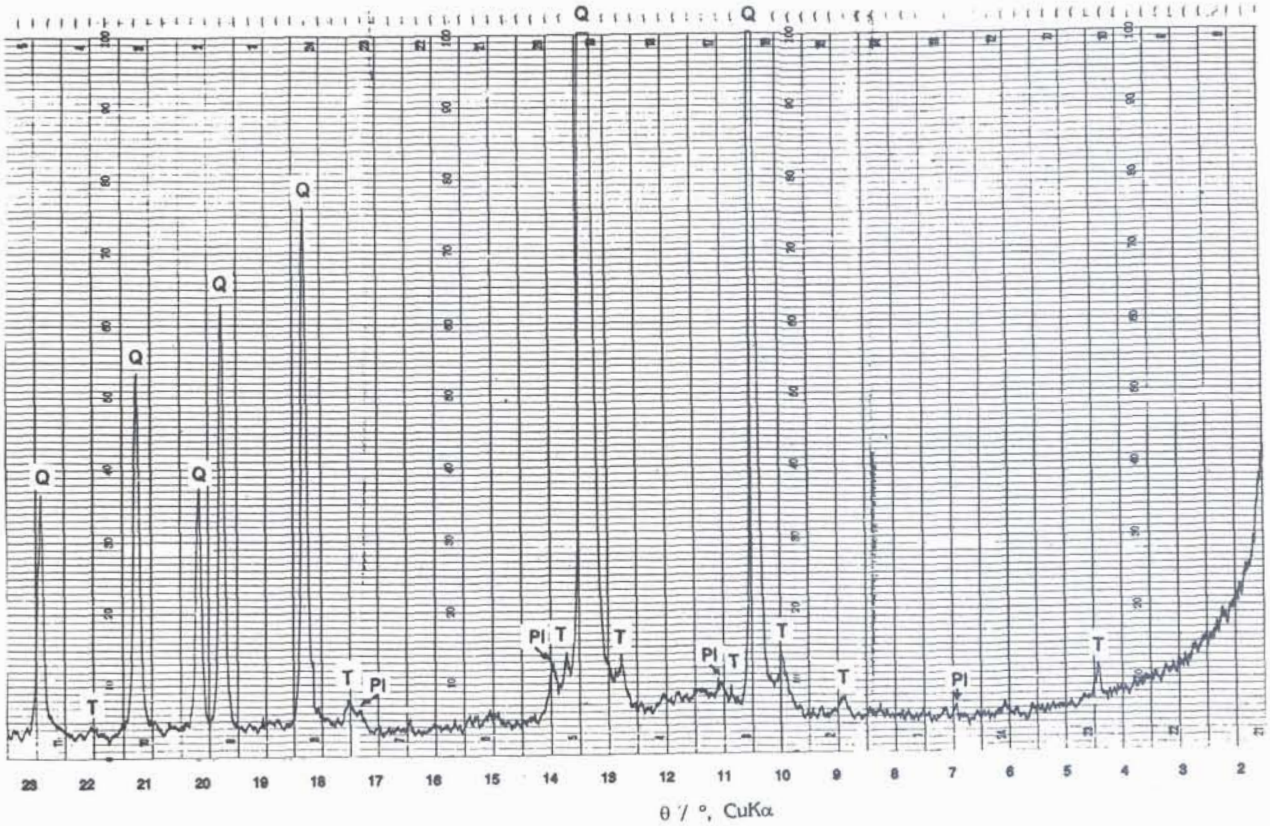


Fig. 16. X-ray diffraction powder patterns of insoluble residue od black scab

The same samples were examined by applying thermal analysis. The thermal analysis were performed under the following conditions: scale DTG 1/10, scale DTA 1/10, sensitivity Tg 500 mg, initial voltage 115 V, photographing interval 100 min.

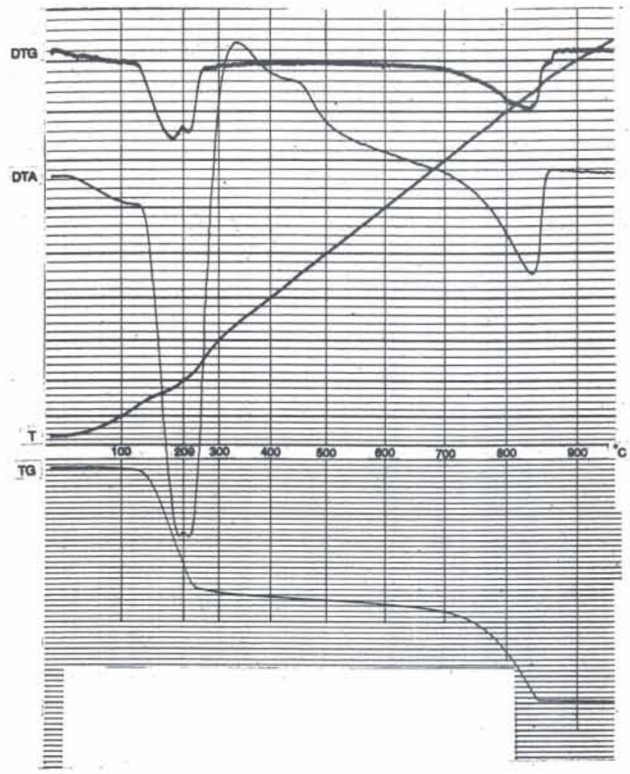


Fig. 17. Thermoanalytical curves of black scab crust

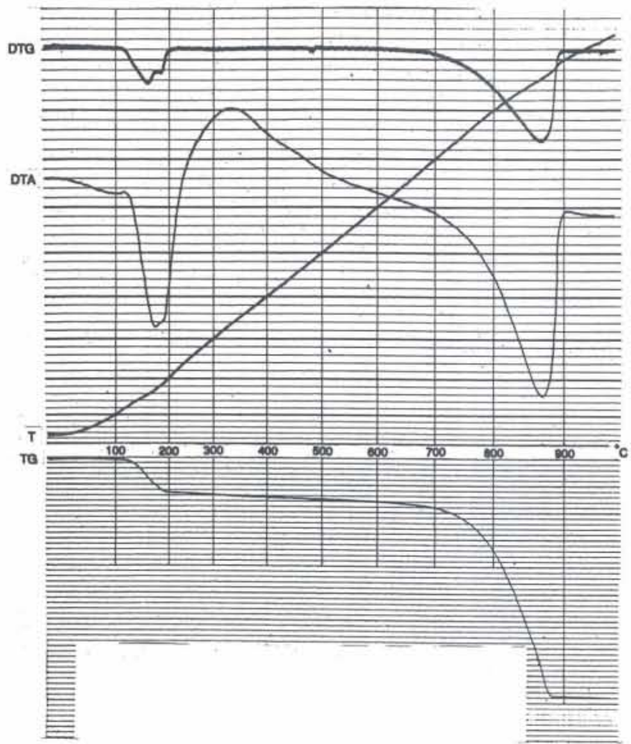


Fig. 18. Thermoanalytical curves of black scab powdery matter

The thermograms (Figs. 17 and 18) clearly show:

— endothermic effects of gypsum dehydrating to a semi-hydrate and loss of the remaining crystal water,
— exothermic effects of restructuring the crystal lattice into anhydrite and combustion of the organic matter of dirt, and
— endothermic effects of calcite decomposition.

Weight percentage of gypsum and calcite in the samples of crust and powder matter obtained in the thermal analyses are presented in Table 2. A histogram in Fig. 19 represents the findings.

Table 2 Approximate weight percentage of gypsum and calcite in the samples of crust and powder matter obtained in the thermal analyses

| Sample | Gypsum (%) | Calcite (%) | Totally (%) |
|---|---|---|---|
| BC | 69 | 24 | 93 |
| BB | 25 | 64 | 89 |
| VC | 70 | 15 | 85 |
| VB | 16 | 66 | 82 |
| S1 | 71 | 19 | 90 |
| S2 | 36 | 52 | 88 |

BC — balustrade, black crust
BB — balustrade, powdery matter
VC — cornice, black crust
VB — cornice, powdery matter
S1 — mixture of samples of balustrade and cornice, black crust
S2 — mixture of samples of balustrade and cornice, powdery matter

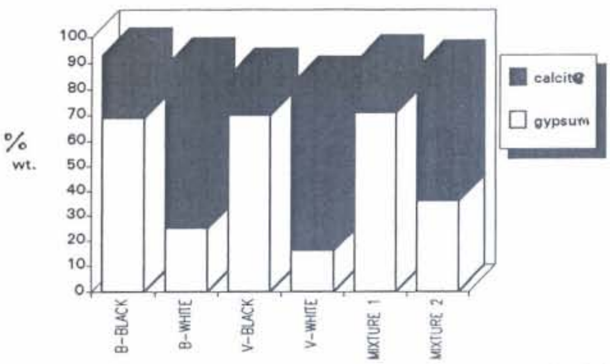


Fig. 19. Histogram of weight percentage of gypsum and calcite in the samples of crust and powdery matter obtained by the thermal analyses
B-black — balustrade, black crust
B-white — balustrade, powdery matter
V-black — cornice, black crust
V-white — cornice, powdery matter
mixture 1 — mixture of samples of balustrade and cornice, black crust
mixture 2 — mixture of samples of balustrade and cornice, powdery matter

Two components were examined by means of quantitative chemical analysis, which contained the following in equal measure:

1) crusts of the black scabs taken from the cornices and balustrade on the northern and western sides of the gallery, and
2) powdery matter from between the crusts of the same samples as under 1.

Results of the chemical analyses are presented in Table 3.

Table 3 Chemical composition of mixture 1 and 2

| | M−1 (%) | M−2 (%) |
|---|---|---|
| insol. res. | 6.53 | 6.02 |
| $SO_3$ | 30.23 | 15.16 |
| $R_2O_3$ | 1.47 | 1.34 |
| CaO | 34.92 | 43.53 |
| MgO | tr. | tr. |
| wet | 0.22 | 0.18 |
| crystal water | 13.72 | 6.62 |
| $CO_2$ | 10.93 | 26.35 |
| | 98.02 | 99.20 |

M−1 — mixure of samples of balustrade and cornice, black crust
M−2 — mixture of samples of balustrade and cornice, powdery matter

A qualitative chemical analysis was to establish a possible presence of other anions in the black scabs: $Cl^-$, $PO_4^{3-}$ and $NO_3^-$ (chlorides, phosphates, nitrates).

The presence of chloride has been examined through reaction with silver nitrate $AgNO_3$, that of phosphate through reaction with ammonium molybdate $(HN_4)_2MoO_4$, and that of nitrate through reaction with diphenylamine $C_6H_5—NH—C_6H_5$.

Tests conducted to establish the presence of chloride and phosphate were negative, and that of nitrate positive.

On ground of chemical analyses mass percentages were determined of the contents of crust and powder matter of the black scabs presented in Table 4 and in the diagram in Fig. 20.

Table 4 Composition of crust and powdery matter of the black scabs

| | M−1(%) | M−2(%) |
|---|---|---|
| gypsum | 65.0 | 32.6 |
| calcite | 24.8 | 59.9 |
| insol. res. | 6.5 | 6.0 |
| $R_2O_3$ | 1.5 | 1.3 |
| wet | 0.2 | 0.2 |
| | 98.0 | 100.0 |

M−1 — mixture of samples of balustrade and cornice, black crust
M−2 — mixture of samples of balustrade and cornice, powdery matter

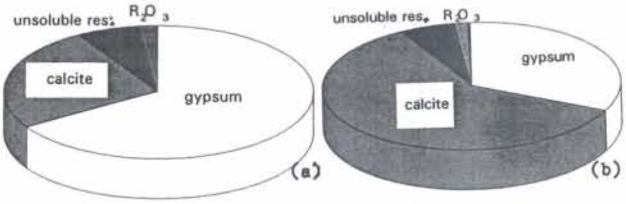


Fig. 20. Composition of the black scabs on cornice and balustrade:
a) — black crust
b) — powdery matter

## Concluding discussion

Religious and secular stone monuments of culture are exposed to the destructive influence of acid rains and other products of techno-zone. The corrosive influence is particularly pronounced in buildings constructed with stone of carbonate composition or those that are covered with it, but also on buildings covered with lime plaster.

Facts about the decay of cultural heritage have been presented at a number of congresses and symposia of restorers and conservationists, including also experts in related sciences, as well as in a large number of published articles and books. Our researches on the influence of acid rains on lithothamian limestone built into the Zagreb Cathedral have corroborated the experience and complemented it with new evidence. In the present discussion we have not considered the origin of the acid rain, to what extent it was produced by the Croatian industry, electric plants, automobile and railway transport, and households, and to what extent was the rain »imported«. The fact is, that the rain causes the development of gypsum on buildings covered with the stone of carbonate composition.

The damaged stone elements show two kinds of corrosion depending on the exposure of their surfaces to moisture and rain.

Parts of stone elements drenched by rain are usually pulverized, flaked or cracked in varying degreees. Such parts do not contain any substanital amount of gypsum. The gypsum that develops on the exposed stone elements dissolves and is washed away. In this manner the stone elements gradually become thinner. This can be especially clearly noticed on the gallery balusters (Fig. 8). Depending on the quality of the stone they were cut from, some balusters are affectd by corrosion described above in such a degree as to have become thin and stripped down to the shaft by which the balusters are anchored at the foot of the balustrade.

On the surfaces of those parts of the stone elements that are in the »shade« three types of calcium sulphate black crusts or scabs have developed. The form of this black crust and scab depend on the characteristics of the stone. The black crusts closely adhere to the stone surface of the lithothamnian limestone from the quarry in Bizek, which has favourable physical and mechanical properties. On the silty lithothamnian limestone of poorer properties, which is obtained from the quarry in Vrapče Potok, the black crusts peel and fall of the stone surface from time to time. Such stone elements with black crusts and scabs mar the appearance of the gallery by gradual peeling and lose of their original shape.

The description of the state of stone elements of the gallery, the console cornices and the balustrade shows that the suggested restoration work is both, logical and acceptable. It is to replace all stone elements in the gallery by newly cut ones. The stone is to be replaced by travertine, which resembles the lithothamnian limestone in both colour and appearance. Its physical and mechanical properties are, however, superior and experience has proved that it is more durable in the polluted atmosphere of an urban environment.

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