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PRELIMINARY RESULTS OF DEGRADATION OF THE STONE ELEMENTS BY ATHROPOGENIC AIR POLLUTION IN THE HISTORIC BENEDICTINE ABBEY AT TYNIEC NEAR CRACOW

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Abstract: The research included qualitative and quantitative determination of atmospheric pollution in Tyniec near Cracow and its effects on stone elements of the local abbey buildings. Samples were studied using optical (in transmitted light) and scanning microscopy, X-ray and chemical analyses. It has been established that the dust is composed of quartz, accompanied by small amounts of feldspars, micas, heavy minerals, carbonates (all of them are natural components), while gypsum, anhydrite, spherulitic forms of iron oxides and combustion-derived glass, chlorides and carbonates are anthropogenic components. Stone surfaces are additionally covered by a black crust, composed mainly of gypsum and enriched in heavy metals: Zn, Cd, Pb, Ni, Cr and Cu. The extent and type of stone damage have been preliminarily evaluated.

Key words: air pollution, Cracow monuments, stone degradation.

Introduction

Tyniec, one of the neighbourhoods of Cracow, is situated in the western part of the city, some 12 km from the centre. The Benedictine Abbey in Tyniec near Cracow was established by French monks in 11th century. The monastery is built of Carpathian sandstones, Jurassic limestones, and bricks. Outer decorative elements have been made of sandstones and Pińczów limestone, and inner elements of the black Dębnik limestone. The abbey towers immediately over the Vistula River, being erected on a strongly carstified, Jurassic monadnock. Tyniec Abbey is a first class architectural monument.

The analyses were carried out in laboratories of the Department of Mineralogy, Petrography and Geochemistry, University of Mining and Metallurgy in Cracow.

Cracow is one of the most ecologically endangered towns in Europe. Its air circulation is very poor, with a characteristic, high number of windless days — 28 %. The low insolation of Cracow, only 37 %, and its humidity as high as 80 % cause of frequent fogs. Temperature inversions are frequent and they cause temporary increases of pollutants (Haber 1990) exceeding many times the normative values.

The area of Cracow Voivodeship represents 1% of the territory of Poland, but receives ca. 5 % of dust (5th most polluted area in Poland) and 8 % of the gaseous emissions (3rd most polluted area in Poland). The data for the city of Cracow are still worse — among the towns with populations over 100,000, Cracow is the most polluted with dust (16.400 mg) and gases (185.000 mg) and 4th most polluted with SO_2 (31.800 mg) (Turzański 1993; Wojewódzki ... 1995, 1997). The amounts of polluting materials emitted to the atmosphere over Cracow during 10 years (1987-1996) are presented in Table 1. The negative impact of a given airborne chemical substance on historic buildings depends on its concentration in the air and duration of exposure. The main sources polluting the air in Cracow include: industry (mainly metallurgy), power generation, municipal engineering, transport. Their impacts are aggravated by a poorly developed system of green areas (Turzański 1993). The major pollutants are: NO_x, CO, SO_x, fluorine compounds, suspended particulates, aromatic and chlorinated hydrocarbons, organic solvents (Gumińska 1990, Manecki & Marszałek 1993). The most common elements of dust contaminating the atmosphere over Cracow are presented in Table 2.

Limestones and sandstones with calcareous cement, used in construction of the monastery buildings, are particularly sensitive to the action of SO_x and NO_x, the gases which under wet conditions react with $CaCO_3$ altering it into gypsum. Gypsum has much less mechanical strength and its presence leads to crumbling of stone elements. The intensity of this process depends on:

— climatic conditions,

— the kind and concentration of pollutants,

— duration of exposure to pollutants,

— the kind of exposure of the stones to atmospheric agents and dust contaminants enhancing stone decay processes,

— structures and textures (porosity) of rocks (Manecki et al. 1982; Haber 1990).

Table 1: Dust and gases emission in the period 1985-1996 on the basis of data of Regional Authorities, Regional Inspectorate of Environment Protection and industrial enterprises in Cracow [× 1000 t./ year].

YEAR	DUST	GASES				
		SO_x	NO_X	CO	OTHERS	TOTAL
1987	111.1	101.7	49.3	405.5	34.3	596.0
1988	101.4	93.8	46.1	378.4	34.3	552.6
1989	95.6	94.3	42.6	405.4	33.1	575.4
1990	69.0	67.1	44.3	295.6	25.8	432.8
1991	44.2	57.5	31.6	163.5	19.9	272.5
1992	34.2	50.5	23.0	127.8	8.7	210.0
1993	24.1	49.6	22.4	142.7	1.4	219.5
1994	20.0	50.6	22.2	147.7	2.0	224.8
1995	20.9	60.8	27.0	145.4	3.7	236.9
1996	17.6	53.2	25.8	77.3	3.4	159.8

The historic complex of Tyniec Abbey has been damaged by the polluted atmosphere in the same way as buildings in the centre of Cracow. In 1966 extensive restoration of the church was initiated, including its architecture, wall painting and inner equipment, as the state of these objects required complex conservation. From outside, the roof of the church and the towers were repaired in 1966 and the western elevation in 1969-1973. At the end of 1980-ties the outer part of the church had to be repaired and renovated again. The cause of the damage was identified as air pollution, caused by emissions from several plants, situated in the proximity of Tyniec: the Aluminium Plant in Skawina and the Soda Solvay Works in Cracow. Compounds of fluorine and calcium contained in the dust particles were particularly damaging to stone and ceramic elements. The most severely affected were the roofs of the buildings, the church elevations and the stone statues of St. Peter and St. Paul from the western façade. Roof and tower tiles, partly replaced in 1966, were strongly damaged (scaling and dampening), crumbling step by step and being pervious to rainwater after 20 years of use. There were numerous losses of stone and mortar on walls, while the statues of church patrons, carved in Pińczów limestone, displayed much damage of a physical and mechanical nature. The latter were particularly grave, as rains and snows, cumulating air pollutants, permeated the stone structure and caused its disintegration. The accelerated process of stone decay has been on the rise for the last 35 years (Detloff 1995).

Methods

Investigations of atmospheric pollution, started in 1995, were conducted on the basis of analyses of dust particles. Atmospheric dust samples were collected during seven consecutive months from June to December, and stone elements were sampled from abbey walls, made of Jurassic limestones and sandstones. The atmospheric dusts were sampled during two periods: summer, encompassing the months of June-September and winter, i.e. October-December. The samples of dusts obtained with sedimentary methods were multiphase systems and before further analyses they had to be separated into fractions easy and difficult to dissolve in water. The collected samples of rainfall were filtered with a strainer in order to separate relatively large organic particles (leaves, insects etc.). The rainfall with dusts was divided into two parts, respectively easy and difficult to dissolve in water, the latter being separated after 48 hours sedimentation. Then, using careful decantation, the solution containing easily soluble atmospheric dusts was obtained. The next step was the water evaporation and drying of dusts at a temperature of 60 °C. After this procedure, the water soluble with difficulty part of the sample contains dust particles, whereas the easily soluble part is the dry residuum of rainfall containig soluble, crystalline compounds and very tiny dust fraction (below 1 μm), not sedimenting but suspended in the rainfall sampled. In order to remove the organic matter the soluble with difficulty parts were burned at a temperature of 450 °C, obtaining the so called mineral dust. The organic matter, being amorphous, has negative effects on X-ray diffractograms and makes microscopic views obscure.

The scheme of separation (Manecki 1976):

atmospheric rainfall (rain, snow) with dust
sedimentation (48 hrs)
↓
followed by decantation of solution
↓ ↓

part difficult to dissolve in water (dusts)	part easily soluble in water (water solution)
↓	↓
drying (60 °C)	evaporation
↓	↓
part insoluble in water (dust)	part easily soluble in water (dry precipitated residuum)
↓	
burning (450 °C) (removal of organic matter)	
↓	
mineral dust	

Table 2: Most common constituents of dust in atmosphere of Cracow (A. Manecki).

Quartz SiO_2	natural & anthropogenic
Gypsum $CaSO_4\,2H_2O$	anthropogenic
Hematite Fe_2O_3	anthropogenic
Magnetite Fe_3O_4	anthropogenic
Mullite $Al_6Si_2O_{13}$	anthropogenic
Calcite $CaCO_3$	natural & anthropogenic
Aluminosilicate glass	anthropogenic
Graphite C	anthropogenic
Unburned parts of coal	anthropogenic
Organic matter	natural & anthropogenic
Micas (aluminosilicates)	natural & anthropogenic
K-feldspar $KAlSi_3O_8$	natural & anthropogenic
Plagioclase (Na-Ca aluminosilicates)	natural & anthropogenic

Two-pronged field investigations were carried out in 1995: dust and rain falls were collected to measure pollution of the atmosphere, and samples of stone elements from the abbey walls were taken to assess damage to them. Laboratory studies included optical microscopy (quantitative and qualitative measurements with counting of grain mounts), scanning microscopy (SEM) — samples covered with graphite, X-ray (XRD) analyses — DSH method, chemical determinations (using AAS) — dust analysed was dissolved in acids.

Results

1. Dusts

The rains in Tyniec have a weakly acid reaction: the pH of samples collected during the seven months (June to December) varied between 4.61 and 7.38 (see Table 3). The annual dustfall was 36 t/km^2/year. Out of that, almost 30 % is composed of organic fragments (remains of plants and insects). Ca. 50 % of the dustfall is represented by components easily soluble in water which are the most deleterious to the environment, because they enter geo- and biochemical cycles being sorbed by soils and elements of constructions and assimilated by living organisms. Detailed data are presented in Tables 4 and 5. Precipitates obtained after evaporation of rainwater are composed mainly of gypsum and anhydrite, accompanied by chlorides and carbonates. All these compounds have been considered to be of anthropogenic origin. They are most often represented by spherical or tabular, sometimes irregular grains of iron oxides (magnetite, hematite), spherical forms of aluminosilicate glass from coal combustion and so called „cokes" — residues of unburned coal. The main constituent of dusts of natural origin is quartz, significantly prevailing over feldspar, micas and heavy minerals (zircon, rutile) and carbonates. Natural particles represent 21-31 vol. % in that group of dusts (Figs. 1, 2). The dusts falling on the Tyniec area contain such elements as: Fe, Mg, Ca, Na, K, Zn, Pb, Cu, Ni, Al and Ti, being almost identical in composition with the dust emitted by the industries of Cracow (Marszałek 1992). The dust from Tyniec does not contain Mn, whereas Al and Ti are present, most probably from long-distance emissions (Manecki & Marszałek 1993). Enrichment of the outer parts of the examined sandstone and limestone in heavy metals is due to industrial emission of dust.

Apart from industrial and power plants, during the winter period an important part of the air pollution, ca.

Table 3: Average monthly pH.

MONTH	VI	VII	VIII	IX	X	XI	XII
pH VALUE	6.90	6.37	4.61	4.83	6.45	6.21	7.38

Table 4: Dust precipitation in [t/km^2/month].

MONTHS\	VI	VII	VIII	IX	X	XI	XII	TOTAL
PERIOD	SUMMER				WINTER			
DUST ELEMENTS								
dust hardly soluble in water	1.50	1.54	0.97	1.28	1.51	1.01	2.57	10.38
dust soluble in water	1.65	1.23	0.09	1.22	2.32	0.64	3.41	10.56
total fallout	3.15	2.77	1.06	2.50	3.83	1.65	5.98	
	9.48				11.46			20.94
mineral dust	2.76				3.47			6.23
dry precipitated residuum	2.59				1.08			3.67
organic matter	4.13				6.91			11.04

Table 5: Percentage [in wt. %] of soluble and hardly soluble in water dust.

MONTHS/	VI	VII	VIII	IX	X	XI	XII	TOTAL
PERIOD	SUMMER				WINTER			
DUST ELEMENTS								
dust hardly soluble in water	47.6	55.6	91.6	51.2	39.3	61.1	42.9	49.6
	55.8				55.6			
dust soluble in water	52.4	44.4	8.4	48.8	60.7	38.9	57.1	50.4
	44.2				44.4			
total fallout	45.3				54.7			100.0
mineral dust	29.1				30.3			29.8
dry precipitated residuum	27.3				9.4			17.5
organic matter	43.6				60.3			52.7

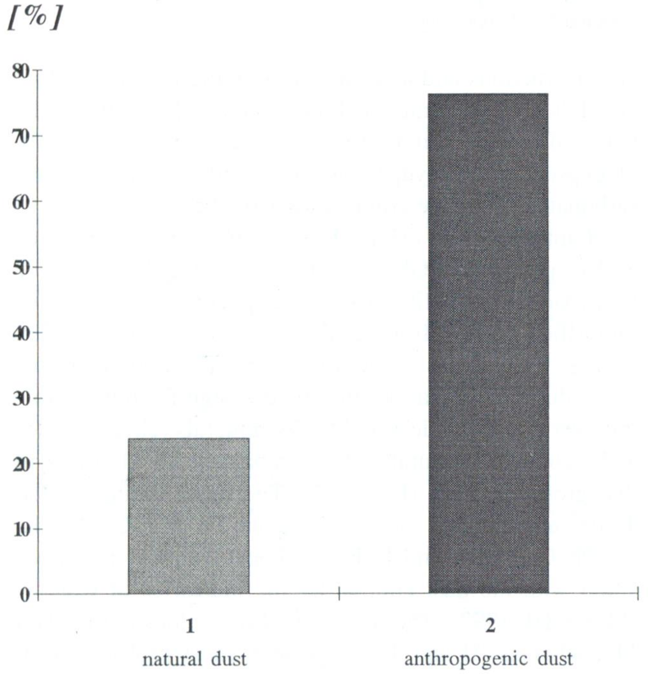

Fig. 1. Percentage of natural and anthropogenic dust during the summer period.

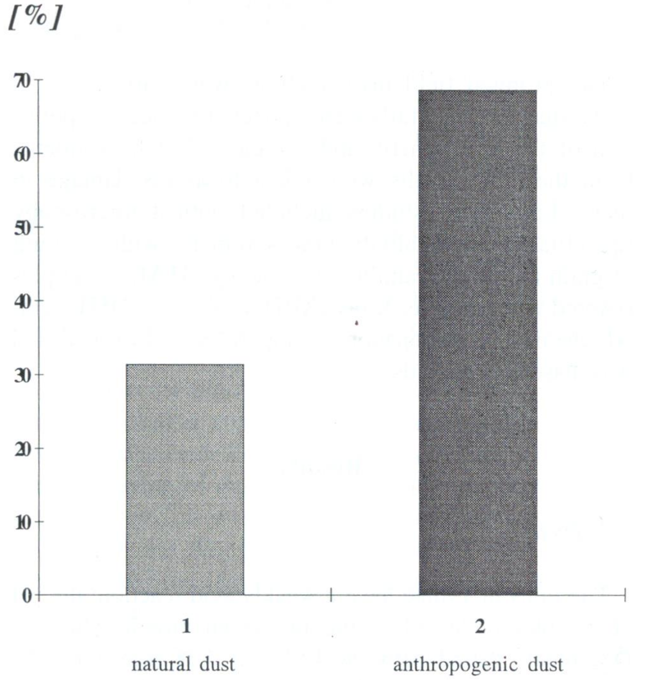

Fig. 2. Percentage of natural and anthropogenic dust during the winter period.

40 %, comes from local boiler rooms and domestic kitchens, operating with coal (Manecki & Marszałek 1993). In Tyniec, where many houses are heated with individual coal boilers, even a larger part of the pollution orginates in this way. It is reflected in the examined samples of dust: the amount of „cokes", soot particles and mullite is much larger in the winter period.

2. Stone elements

The first mineralogical investigations on the deterioration of the stone elements of monumental buildings in Cracow were carried at the Department of Mineralogy, Petrography and Geochemistry, University of Mining and Metallurgy in Cracow, under the direction of Prof. Andrzej Manecki (Manecki et al. 1982).

The investigations performed enabled preliminary determination of changes in stone elements of the abbey. Some of these changes could be connected with natural weathering processes, but most of them are caused by action of the polluted atmosphere on the stone surface. The surface is covered with black or dark grey crust, often peeling off. It is different from natural patina, formed as a result of mineralization of the outermost part of the rock. The natural patina brings about consolidation of the external layers of the material without affecting the free exchange of humidity between the air and the stone. The layer observed on the samples examined does not protect the material, being the weakest one, and the first to peel off. In this way, the next, also weakened layers of stone are exposed to the destructive agents. The stone conservators describe layers of such black or grey crust as a „false patina" (Marszałek 1992).

The external signs of damage are different in limestones and sandstones. The former are more damaged: the crusts are cracked and exfoliated from the inner part of the stone. Under the crust, the stone is loosened and crumbles because its carbonate and carbonate-clay cement is washed out. The formed layer of „false patina" does not protect the stone. Sealed mainly by hydrated sulphates and dusty pollutants, it stops migration of soluble salts from internal parts of the stone and prevents their crystallization on the surface. This results in destruction of near-surface layers, cracking and peeling off of successive outermost layers, exposing the internal ones. Limestones are covered by compact crusts while their inner parts are rather well preserved (Marszałek 1995).

The patina is composed of poorly crystallized gypsum (see Fig. 3), glass spheres, coal particles and spherical aggregates of iron oxides (see Fig. 4), all of them of anthropogenic origin. Elements found include Fe, Ti, K, Al, Ca, Na, Cu, Zn, S, Cl and Si. Sulphur present in the chemical composition of the „false patina" occurs as in sulphate ions formed in reaction of SO_x emitted into the atmosphere with rainfall synthesis of H_2SO_3 and H_2SO_4 acids. According to many conservators, it is SO_2 that is particu-

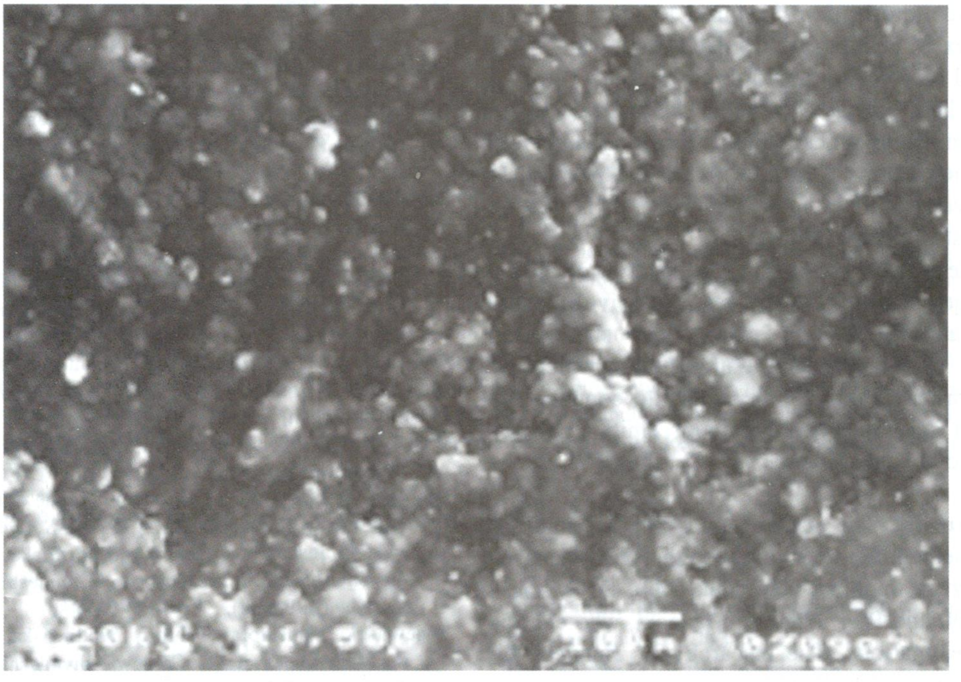

Fig. 3. Poorly crystallized gypsum in the „false patina" from the surface of the limestone.

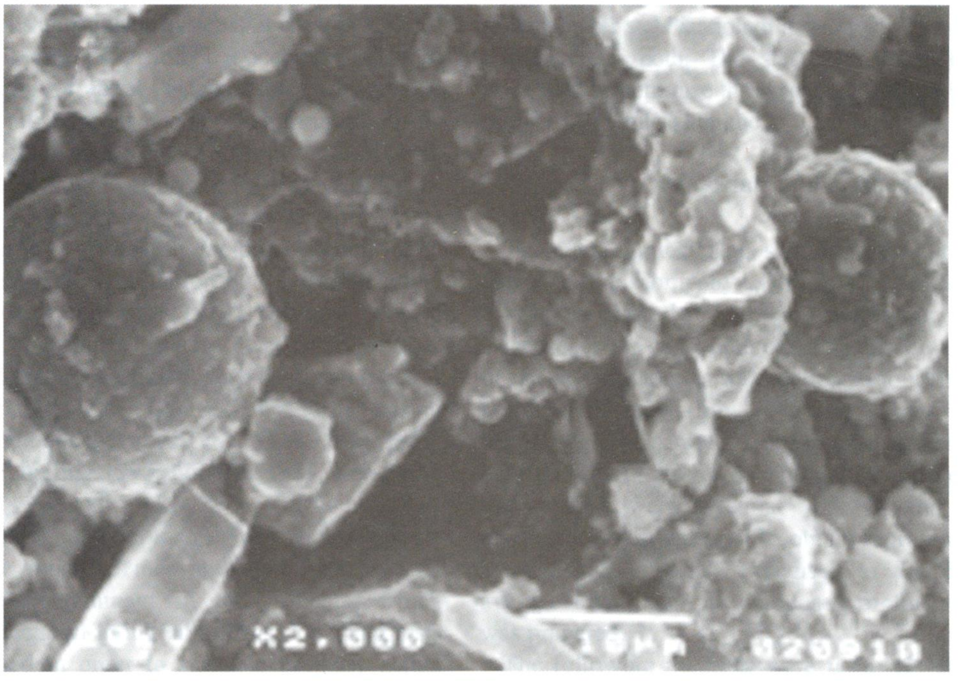

Fig. 4. Aluminosilicate glass spheres, and spheres and tables of iron oxides in the „false patina" from the surface of the sandstone.

larly responsible for corrosion of stones. Sulphuric acid solutions migrate to the inner parts of the rocks, transforming calcium carbonate into hydrated calcium sulphate (Ślesiński 1990).

Conclusions

In the last century a rapid acceleration of deterioration of stone monuments in Cracow has been observed. Many conservators link this phenomenon with the development of industry and motorization (Ślesiński 1990).

The complex of buildings of the Benedictine Abbey in Tyniec should be further studied. From 1957 to 1981, an aluminium plant, situated several kilometres away, emitted fluorine compounds, which strongly affected natural and artificial stone elements. An active power-heat plant, also adversely affecting the environment, is situated at the same distance from the abbey.

Despite a decreasing trend in contamination of the air by dusts and gases in the Cracow area, excessive amounts of SO_x, F and particulate matter are still noted (Wojewódzki ... 1995, 1997). Putting the problem of stone conservation aside, it is necessary to continue the modernization of industry — the major emitter of contamination into the atmosphere.

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