4. Air pollution and damages to the cultural heritage in cities

The decay of the cultural heritage of Kraków

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4.1 AIR POLLUTION IN KRAKÓW

4.1.1 A history of air pollution

Kraków is a city troubled by air pollution. Smoke and sulphur dioxide from combustion of black coal in industries and homes dominated earlier, today the traffic is a major source. Data published by the Central Statistical Office (Ochrona Środowiska, 2000) indicate that Kraków still ranks in the top ten of cities in Poland seriously threatened by air pollution.

Air pollution is aggravated by the situation of the city in a valley, and the prevailing climate of low wind velocity, a high number of foggy days and nights, and temperature inversions. Kraków is a poorly ventilated city with numerous narrow, "canyon" streets with high buildings.

The predominance of western winds brings pollution from Upper Silesia, the largest industrial agglomeration in Poland situated about 30 kilometres from Kraków, and from abroad. An important source of air pollution is Skawina S.A. Power Plant located 15 kilometres to the southwest of the city. It has been assumed that imported pollution sometimes accounts for 47% of the air pollution in Kraków (Raport o stanie. 1995)

Although the consumption of electricity in households is still growing, particulate and gaseous emission from the Elektrocieplownia Kraków S.A. (a combined heat and power plant) and the municipal district heating company dropped since the late 1990s. The Elektrocieplownia Kraków S.A. power plant reduced its gas and dust emissions by 22% and 33% respectively, and the municipal district heating company reduced its gas and particulate emission by 2% and 26%. The improvements were due to modernisation of the ash retention tanks and the automation of technological processes (Pajak, 1999).

KRAKOW

Kraków is situated in upper Wisla Valley in southern Poland. Its legendary founder, King Krak, is believed to have lived in the early 8th century. Through its more than thousand year long history Kraków has had a central position in Central European politics and culture. It was the capital of Poland up to the end of the 16th Century. It is the home of the Jagellonian University, one of the oldest insitutions of higher learning on the continent.

Although Kraków was always a city of studies and trade, after World War II, it was, by the communist regime, increasingly industrialised mainly with metallurgical and chemical manufacturing industries.

Each epoch of the over thousand years long history has been rich in historic monuments. In 1978 Kraków was given UNESCO status of world heritage. After the systems change and the so-called Round Table in 1989 Kraków was one of the first cities in Poland to be granted "most-protected-city" status.

At present, Kraków occupies an area of 327 km^2 and has a population of 800,000 – out of which approximately 100,000 are students of universities.

Figure 4.0 Wawel Royal Castle has been home to three dynasties of Poland's monarchs. Its stately halls and exquisite chambers are filled with art and period furniture.

Krakow's central Grand Square (Rynek Glowny) is the largest plaza of medieval Europe and it has remained the hub of the city since the 13th century.

In the city centre harmful substances in the air have decreased, as the furnaces in the homes have been modernised and coal exchanged for e.g. gas or oil. Simultaneously the consumption of gas is decreasing slowly.

However traffic is increasing. The number of road-vehicles in Kraków (Table 4.1) and heavy traffic, exceed 4,000 vehicles per hour on some of the transport routes. The highest concentrations of traffic-related air pollutants recorded in 1994-98 were nitrogen dioxide: 61-68 mg/m^3, carbon monoxide: 2,400-3,500 mg/m^3, benzo(a)pyrene: 6.7-13.3 mg/m^3 and particulates [PM10]: 72-86 mg/m^3. The average annual concentration of lead and cadmium in particles exceeded permissible standards (Pajak, 1999).

4.1.2 Origin of air pollutants

Gaseous emission from power plants in the Kraków area and in Upper Silesia accounts for about 20% of the total gaseous emission in Poland. Sulphur dioxide emissions from heat and power plants in Poland is a major casue of the deterioration of stone. Pollution emitted by the Sendzimir Steelworks still contributes significantly to the amount of industrial pollution in Kraków.

Emission of dust from fuel combustion varied between 49% (in 1990) to 56% (in 1999) of the total dust emission in Kraków for the period 1990-1999 (R. Statystyczny Krakowa, 2000). In the mid 1990s dust and gaseous emission from power plants in Kraków increased because of the increased production of energy.

During 1998-99 emissions from Šlaskie, Malopolskie and Podkarpackie voivodeships (Table 4.2) had a crucial share in the total emission of pollution: 63.0-88.9% of dust, 93.5-98.5% of sulphur dioxide, and 72.6-92.3% of nitrogen oxides (O. Šrodowiska, 2000). In the Malopolskie voivodeship carbon dioxide emission reached 12,500 thousand tonnes in 1999. 71% came from the municipal heating enterprise and private coal-fired home boilers/furnaces.

The air in Kraków is polluted by emissions from home furnaces and cars. High emissions of nitrogen dioxide and carbon monoxide from traffic is confirmed by traffic-related pollution monitoring station with automatic equipment (city centre, Krasinskiego avenue), where concentrations exceeded permissible standards were recoreded (Czarnecka, 1999).

In 1998, for the first time in five years, the share of gaseous pollutants in Kraków increased in comparison with particulate emission. This caused the decrease in pH of wet deposition, observed the last few years (Report on the Environment in Kraków 1994-1998, 1999).

Table 4.1 Registered and newly registered road vehicles in Kraków.

Specification	1993	1994	1995	1998	1999
Registered (in thousands)	203.7	215.5	226.3	270.4	286.3
Registered/100 households (in thousands)	64	67	70	83	87
Registered/1000 residents (in thousands)	231	243	253	301	317
Newly registered (units)	14,377	14,782	15,598	18,078	21,861

(Source: Rocznik Statystyczny Krakowa, Urzad Statystyczny w Krakowie, Kraków 2000; 2000 Statistical Paper of Kraków 2000, Statistical Office of Kraków, Kraków 2000).

Table 4.2 Dust and gaseous emission from major industrial polluters by voivodeships in 1998-1999 in 1 000 tonnes per year (1kt/y). NO_x denotes nitrogen oxide (NO) and nitrogen dioxide (NO_2) together.

		DUST EMISSION			GASEOUS EMISSION									
		Total	Fuel combustion		Total	Total SO_2	SO_2 from fuel		Total NO_x	NO_x from fuel		Total CO	Total CO_2	Total hydro-carbon
Voivodeship		kt/y	kt/y	%	kt/y	kt/y	kt/y	%	kt/y	kt/y	%	kt/y	kt/y	kt/y
Šlaskie	-98	54.9	41,4	*75.4*	35,776.5	207.3	198.1	*95.6*	87.1	79.1	*90.8*	136.5	35,281.6	55.7
	-99	42.8	34.6	*63.0*	33,951.8	199.5	192.6	*96.5*	79.7	73.6	*92.3*	117.5	33,361.7	192.1
MaĦ	-98	20.6	16.2	*78.6*	13,714.4	76.9	71.9	*93.5*	30.4	25.2	*82.9*	56.6	13,492.1	56.5
opolskie	-99	16.6	13.0	*78.3*	12,956.1	64.5	59.9	*92.9*	29.4	24.2	*82.3*	49.1	12,533.7	52.8
Podkar-	-98	7.2	6.4	*88.9*	3,830.3	20.3	20.0	*98.5*	8.8	7.1	*80.7*	9.1	3,790.5	1.2
packie	-99	5.2	4.5	*86.5*	3,565.0	18.3	17.9	*97.8*	7.3	5.3	*72.6*	5.0	3,533.0	1.0

(Sources: Ochrona Srodowiska; Information and Statistical Papers; Environment 1999. Ochrona Srodowiska; Information and Statistical Papers; Environment 2000)

4.1.3 The formation of air pollutants

Pollution from the emissions from combustion of fossil fuels remains a major environmental issue, with health and material damage effects well documented (Kaupplnen & Pakkanen, 1990; Boix et al., 2001; Hewitt, 2001).

Coal is the basic fuel utilised in Poland, both in industrial energy production and in many homes. The main elemental components of fossil fuels are carbon and hydrogen. When burnt with oxygen present in air, carbon is converted to carbon dioxide and hydrogen to water vapour. Sulphur dioxide arises from the sulphur present in most fuels.

Combustion of coal in power plants and home furnaces is a source of sulphur dioxide, nitrogen oxides, ash dust and some soot. The relatively low temperature of coal burning in private home furnaces, causes emission of soot and tarry substances. These have essentially been distilled from the coal and re-condensed in the chimney flue. Such material contains potentially toxic compounds e.g. benzo(a)pyrene (Clarke, 1996). Formation of soot commonly accompanies carbon monoxide formation and is generally due to an inadequate air supply.

Combustion of fuel oils is a source of soot, which consists of hollow, spherical, carbon particles ranging in size from 50 to 100 μm. Since heavy fuel oils contain sulphur, some of which may be converted to sulphuric acid, an additional problem is the emission of acid smuts (Clarke, 1996).

Incomplete burnout of fuel in petrol engines leads to emissions of significant amounts of carbon monoxide and hydrocarbons. Nitrogen oxide emissions are also high due to the high temperatures of combustion. Lead is emitted in exhauses from cars using leaded gasoline. Considerable amounts of soot is emitted from diesel buses and trucks, under heavy load or acceleration.

The emitted gaseous pollutants tend to oxidise in the atmosphere. In the presence of water and water vapour the overall results are acids: sulphuric acid, nitric acid and carbonic acid. The sulphuric and nitric acids are both watersoluble and rapidly absorbed into water droplets, if present.

Carbon monoxide oxidation is a slow process and the lifetime of CO in the atmosphere is several years. The oxidation rate of SO_2 can be around 2% per hour in urban air and is ten times lower in clean air resulting in an overall lifetime of a few days (Clarke, 1996). Relative humidity (RH) influences sulphur dioxide oxidation rates. Generally, the rate of conversion increases sharply as the relative humidity increases above 70% (Amoroso & Fassina, 1983). The relative humidity of the atmosphere in Kraków is high (Table 4.3), with average monthly RH values in the morning and in the evening often exceeding 80%.

Besides moisture from rain and fog, the relative humidity of the atmosphere in Kraków is a very important source of moisture infiltrating into porous building stones.

Table 4.3 The average monthly values of relative humidity (RH) in the atmosphere (%).

	Year					
	1952 –1985			1992*		
Month	7am hour	12 hour	7pm hour	7am hour	12 hour	7pm hour
January	86	78	84	89	78	83
February	86	74	82	90	70	80
March	85	65	76	86	54	65
April	81	56	70	76	52	63
May	79	55	71	79	51	65
June	79	57	72	76	68	61
July	80	57	73	75	49	63
August	84	58	75	76	40	57
September	88	62	80	89	58	78
October	90	68	83	91	64	82
November	88	77	80	90	69	84
December	87	80	85	91	81	90

* Year with the lowest amount of precipitation in the last 100 years.
Source: Institute of Meteorology and Water Management in Kraków.

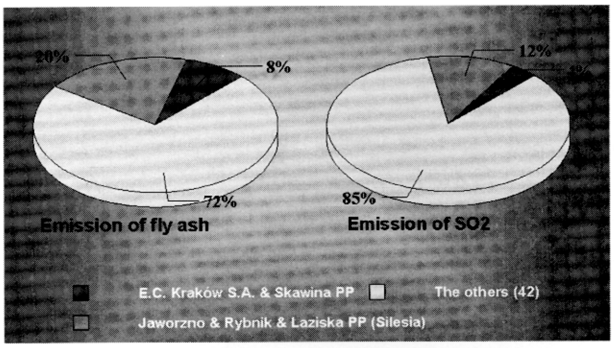

Figure 4.1 Major power plants polluters by quantity of particulates and gaseous emission (1999).

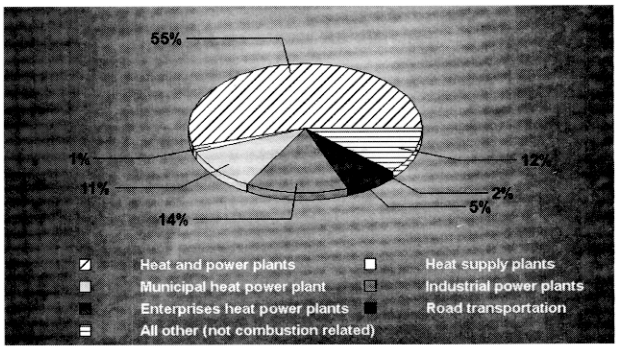

Figure 4.2 Sulphur dioxide (SO_2) emission in Poland in 1988 due to fuel combustion.

4.2 POLLUTING GASES, PRECIPITATION AND PARTICLES

4.2.1 Annual variations

Average composition of atmospheric aerosols in Kraków varies during the year. In wintertime, small carbon-containing particles of soot dominate. In summertime, especially in a dry period, natural soil-derived particles are more frequent. In the period of development of vegetation, biological material is also an important component of aerosols (Kozak et al. 1998).

Large differences in the concentration of air pollution between summertime and wintertime indicate a great influx of pollution from the combustion of fuels (Michalik & Wilczyńska-Michalik, 1998).

The average annual total particulate concentration (TPC) and the average annual sulphur dioxide concentration in the city centre from 1994 to 1998 are listed in Table 4.4. During the growing season, the concentration of SO_2 ranged between 13-22 μg/m³. It was the first time for a number of years that the average annual concentration of SO_2 in Kraków fell below the standard of 40 μg/m³. By 1998 the permissible concentration of sulphur dioxide was more stringently set at 32 μg/m³ (Czarnecka, 1999).

The highest average levels of annual concentration of suspended dust and sulphur dioxide were noted in the city centre in the period 1968 to 1987, when sulphur dioxide concentrations varied from 83 in 1971, to 122 μg/m³ in 1985, and concentration of suspended dust varied from 143 in 1977 to 195 μg/m³ in 1972 (Lach et al. 1996). The average annual concentration of sulphur dioxide in the city centre varied from 122 in 1985 to 75 μg/m³ in 1990 and 1992 (Figure 4.3), and the average annual concentration of suspended dust particles of diameter below 10 μm varied from 116 in 1986 to 52 μg/m³ in 1992 (Figure 4.4).

4.2.2 Precipitation – composition and effects

Precipitation waters in Kraków have a high concentration of minerals (Wilczynska-Michalik et al. 2000). The mineral composition of the dry residue after evaporation of the rain is dominated by gypsum, but sulphates, nitrates, carbonates, phosphates, and chlorides are also found.

The pH of rainwater in Kraków varies within broad limits (4.8-7.1). Most rainfalls have natural to slightly alkaline pH. The average pH value in the close vicinity of Kraków is lower than in the centre of city. The lowest pH occurred in winter, and the highest in spring and summer (Godzik, 1999). From 1994, with a break in 1997 and 1998, the pH of wet deposition has systematically decreased. It is due to a reduction of emissions of dust compared to gases from the industry, as dusts are more alkaline. A gradual acidification of wet deposition may be expected in the future.

Precipitation is an important cause of weathering in Kraków because of the high concentration of pollutants in rain, which causes rock decay by salt crystallisation. The anthropogenic emissions of carbon and sulphur have a much larger acid-generating capacity than natural fluxes. The weathering needed to neutralise these fluxes is far in excess of observed values (Varekamp & Thomas, 1998).

The monthly influx of different chemical components from precipitation was calculated as higher than 1 gram per m². The highest influx of several components does not always coincide with the highest concentration in precipitation (e.g. sulphate ions in June 1998). Recalculation of the influx of calcium and sulphate ions into amounts which can hypothetically precipitate, shows that gypsum may during periods be high (e.g. in November 1998 more than 4 g/m²). The amount of hypothetical gypsum exceeds 3 g/m² per month both in wintertime, when coal-based heating is significant, and in the summertime, when the precipitation is extraordinarily high (Figure 4.5).

Table 4.4

Year	Average annual total particulate (TPC) concentration (μg/m³)	Average annual sulphur dioxide (SO_2) concentration (μg/m³)
1994	38	43
1995	41	42
1996	47	41
1997	37	36
1998	32	28

(Source: Czarnecka, L. 1999. Air quality. In: Report On the Environment in Kraków 1994-1998)

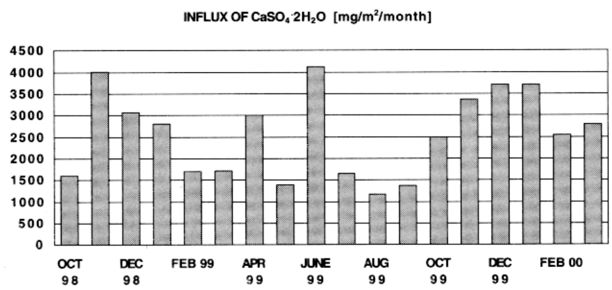

Figure 4.5 The monthly influx of gypsum in Kraków.

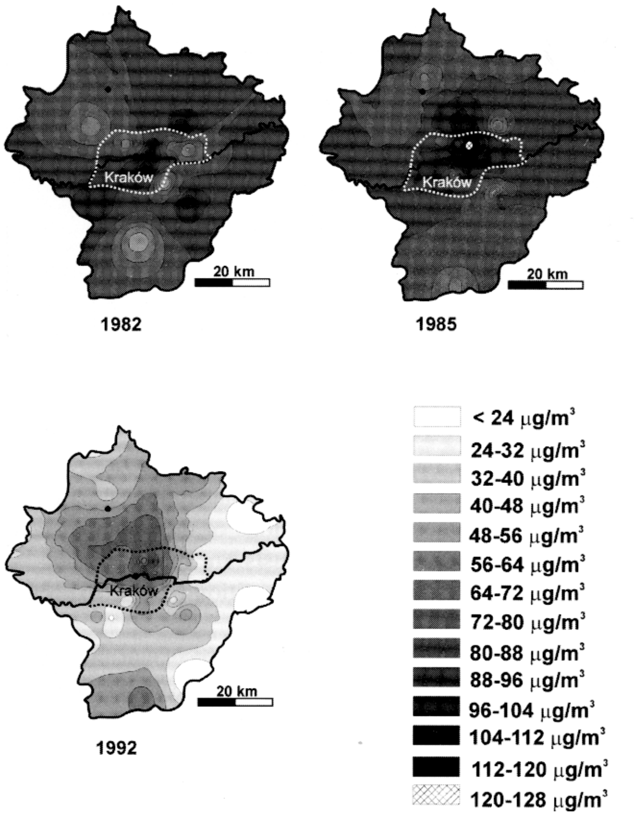

Figure 4.3 The average annual concentration of sulphur dioxide (SO_2) in Krakowskie voivodeship during the period 1982-1992. According to data of the Voivodeship Inspectorate For Environmental Protection in Kraków, 1994.

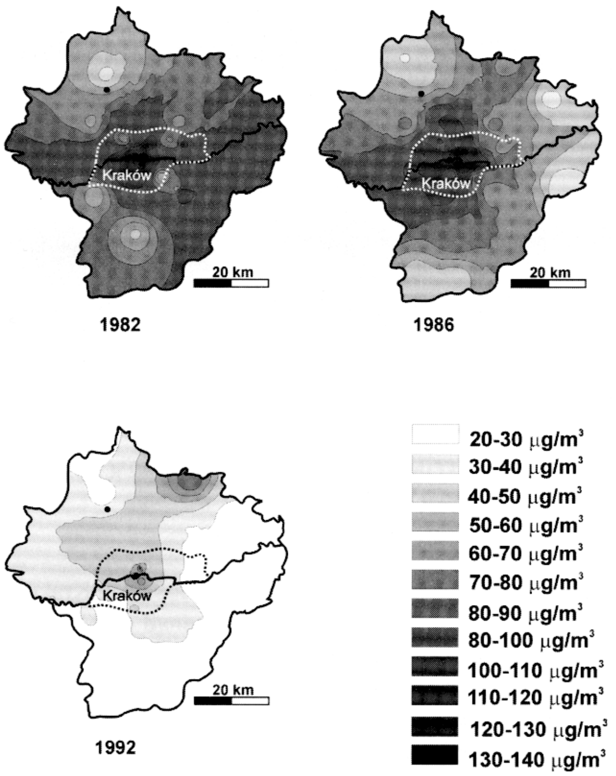

Figure 4.4 The average annual concentration of suspended dust (particles below 10 µm of diameter) in Krakowskie voivodeship during the period 1982-1992. According to data of the Voivodeship Inspectorate For Environmental Protection in Kraków, 1994.

4.2.3 Fly ash and soot particles

Dust from the power plants, that is the fly ash (Figure 4.6), consists of usually spherical amorphous aluminosilicate particles of diameter from <1 to 15 µm. Bigger particles (up to 100 µm) occur rarely. Beside silicon and aluminium, they contain calcium, sodium, and potassium. The content of iron, sulphur, titanium, copper, zinc, magnesium varies in individual particles. The average content of carbon is about 0.5%.

Dust from home furnaces, that is the soot, consists of irregular fine-grained particles less than 1 µm (Figure 4.7). The average content of carbon in the soot samples reaches 45%. Formation of soot commonly accompanies carbon monoxide formation and is due to an inadequate air supply.

Several elements are highly concentrated in the dust in comparison with average sedimentary rocks. The concentrations of bismuth, arsenic, cadmium, lead, and antimony in fly ash are 600; 14; 17; 13 and 11 times higher respectively. In soot the concentrations of selenium, lead, zinc, silver, bromine, cadmium, and bismuth are 150; 24; 44; 20; 125; 85 and 10 times higher (Wilczyńska-Michalik & Michalik, 1998b).

The share of carbon and sulphur in soot is higher as compared with the fly ash from power plants (Figure 4.9).

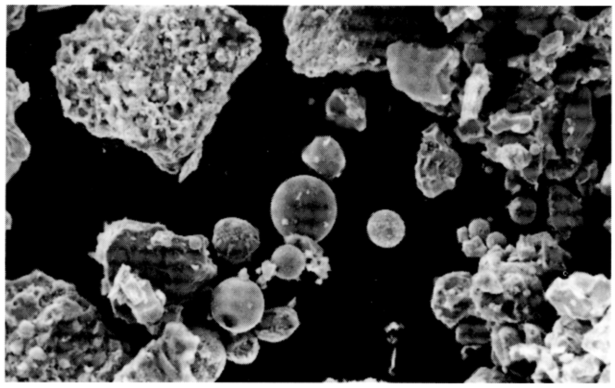

Figure 4.6 Spherical aluminosilicate particles generated by the combustion of fossil fuels (Elektrocieplownia Kraków S.A.). SEM.

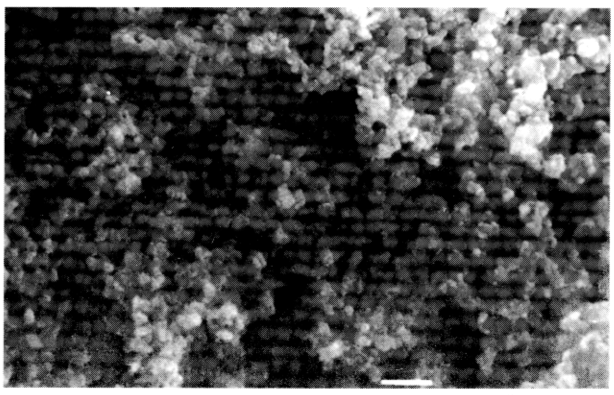

Figure 4.7 Carbonaceous particles (soot) generated by the combustion of fossil fuels from home furnaces. SEM.

Figure 4.8 The strongly damaged sculptures of the Apostles from the 18th century. Photo: Wanda Wilczynska-Michalik.

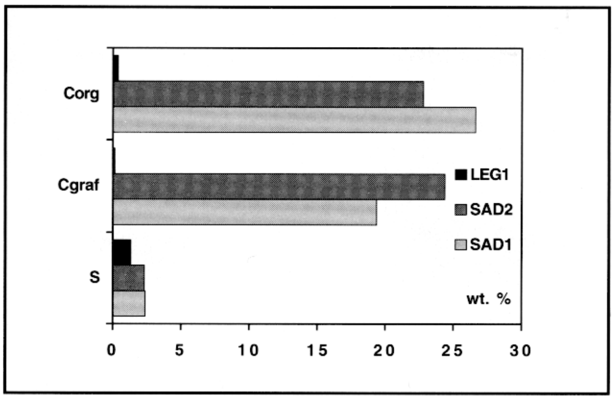

Figure 4.9 Sulphur and carbon ("graphitic" and "organic") in soot from home furnace and fly ash from power plants.

Table 4.5 Minerals present in secondary crusts on building stones in Kraków.

Mineral	Chemical formula
Gypsum	$CaSO_4{\cdot}2H_2O$
Bassanite	$CaSO_4{\cdot}0.5H_2O$
Hexahydrite	$MgSO_4{\cdot}6H_2O$
Epsomite	$MgSO_4{\cdot}7H_2O$
Melanterite	$FeSO_4{\cdot}7H_2O$
Langbeinite	$K_2Mg_2[SO_4]_3$
Mirabilite	$Na_2SO_4{\cdot}10H_2O$
Syngenite	$K_2Ca[SO_4]_2{\cdot}H_2O$
Burkeite	$2Na_2SO_4{\cdot}Na_2CO_3$
Calcite	$CaCO_3$
Dolomite	$CaMg[CO_3]_2$
Halite	NaCl
Sylvite	KCl
Nitronatrite	$NaNO_3$
Nitrammite	NH_4NO_3

6.3 DECAY OF HISTORICAL MONUMENTS IN KRAKÓW

4.3.1 Natural and pollution-caused weathering

Weathering is the process in which stone surfaces are chemically altered or dissolved and washed out as a result of chemical and physical processes. Natural weathering has always occurred. Air pollution may, however, accelerate weathering dramatically. The mechanisms of weathering in a polluted atmosphere differ from the natural ones. Stone decay is caused by the reactions between the components of the rock and the atmospheric pollutants, and crystallisation of new components from precipitation water at the surface and in the pore-spaces of the rock.

Air pollutants in Kraków cause serious damage to historic stone monuments in the city. The decay of building stones is mainly due to sulphuric pollutants, soot, heavy metals, alkanes from petrol combustion, and microorganisms. The stones in the polluted atmosphere show a high degree of surface alteration.

Sulphur dioxide (SO_2) reacts with building materials containing calcium carbonate ($CaCO_3$) to form gypsum ($CaSO_4.2H_2O$), which is by far the most common mineral in the black crusts of damaged stones. Carbon particles, especially those containing trace amounts of metal, are believed to act as catalysts for the oxidation of SO_2 (Sabbioni & Zappia, 1992). The deposition of dusts containing soot, iron and manganese facilitates the formation of a black gypsum crust at the surface of the rock. Rodriguez-Navarro & Sebastian (1996) confirmed in experiments the catalytic role of soot and metal-rich particles from vehicle exhaust has on gypsum crust formation on the surface of limestone.

Both dry and wet deposition of air pollutants is a cause for the deterioration of stonework. The process may be fast. Estimations of sulphur dioxide uptake by limestone show a deposition velocity of several millimetres per second (Amoroso & Fassina, 1983). Overall the dry deposition velocities measured experimentally for sulphur dioxide range from below 5 to nerly 20 mm/sec; a typical value of 10 mm/sec is often assumed (Clarke, 1996).

The solubility of calcite in the rock increases very significantly, by a factor of 100 for each pH unit, with increasing acidity of the solution, with temperature. Increasing carbon dioxide concentrations in the air increase the rate of dissolution of carbonates rocks (Winkler, 1970). The weak acid solution formed by dissolved carbon dioxide in rainwater dissolves the calcium and calcium-magnesium carbonates in limestone and dolomite, as it forms much more soluble calcium and magnesium bicarbonates (Amoroso & Fassina, 1983).

The production of sulphates in clouds could be the major source of atmospheric sulphates (Easter & Hobbs, 1974). Thus formed airborne sulphates dissolve in precipitation water and could be subsequently deposited on stone surfaces.

Microorganisms attack stone by both mechanical and chemical action. Most commonly, the organisms arrive by air, riding on aerosols, particularly soot and via rainwater (Young, 1996).

The historical monuments

The Wawel Cathedral (Figure 4.10) where the kings of Poland were crowned and buried is strongly associated with the history of Kraków and the whole Polish nation. The Cathedral was erected in the years 1320-1364 to replace the former Romanesque churches. The 17th century walls surrounding Wawel Cathedral were built of Libiaż dolomite. Although dating from different periods, all the distinct parts of the Cathedral make a unique and picturesque ensemble.

The fortifications surrounding Wawel hill date from different periods. The first fortifications were built in the early medieval period and are know from archaeological excavations. Defence walls, characteristic for the present Wawel Castle landscape, were built in the14th century (Pianowski, 1991). Fortifications in a neo-gothic style were added in the 19th century. Three bastions are situated at the foothill of Wawel (Pianowski, 1991).

The Church of Saints Peter and Paul (built at the beginning of the 17th century) is considered to be one of the most magnificent early baroque churches in Central Europe. The fence topped with sculptures of the Apostles and enclosing the yard in front of the church is a very characteristic feature of this monument (See Figure 4.11).

The precise date of the installation of the sculptures of the Apostles has been a matter of speculation in the past and in reality we may never know the exact truth. However according to Karpowicz (1985), we can be reasonably confident that the sculptures that decorate the fence in front of the Saints Peter and Paul church are most likely from around 1715-1722. The 18th century sculptures were heavily decayed and now are replaced by copies.

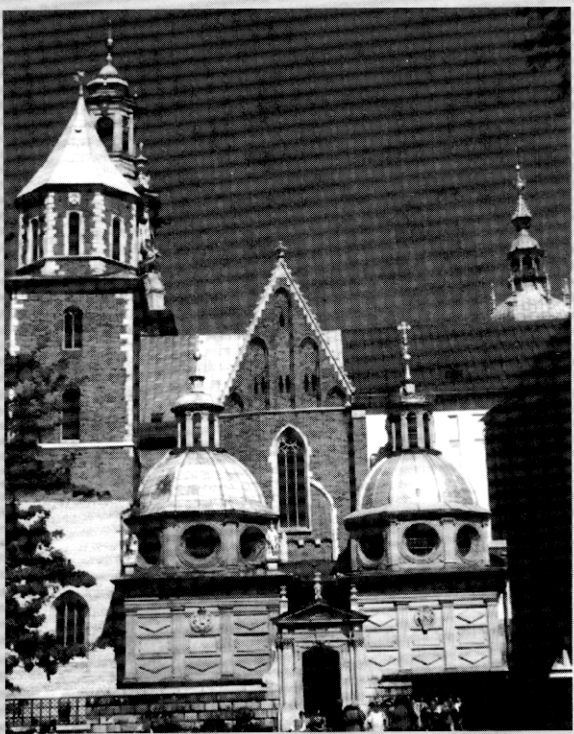

Figure 4.10 The Wawel Cathedral. The Waza Chapel (left) and the Zygmunt Chapel (right). Photo: Wanda Wilczynska-Michalik.

Figure 4.11 The fence of the church of Saints Peter and Paul with the sculptures of the Apostles. Photo: Wanda Wilczynska-Michalik.

4.3.2 Effects on selected building stones

The mechanism and rate of deterioration of different types of stone used as building materials in some significant monuments in Kraków is described in this paper. Particular attention is given to the most characteristic patterns of weathering observed on surfaces of dolomite, limestones and sandstones. The state of deterioration of selected elements of these monuments and results of applied renovation works are included. Results of studies that identify pollution from fuel combustion and pollution derived salts, as the causes of stone damage are also presented.

The durability of various carbonate rocks in the polluted atmosphere in Kraków differs significantly. Upper Jurassic limestone and Pińczów limestone is much used in Kraków's architecture. These two types of limestone show a wide range of durability. Weathering of Upper Jurassic limestones is seen in the 19th century fortifications of Wawel Castle, and of Pińczów limestone in the decayed sculptures of the apostles in front of the of Saints Peter and Paul church.

Upper Jurassic limestone is relatively resistant. Since the Roman period Upper Jurassic limestone has been commonplace in Kraków architecture. It was quarried in some places near the old town or exploited as boulders from the Wisla river alluvia. Upper Jurassic (Oxfordian) limestone is a light-grey or light-beige rock. The porosity of Upper Jurassic limestone varies from <2% to 15%, but usually it is below 10%.

Pinczów limestone, commonly used for carving since the Renaissance period, is a higly porous (usually above 35% porosity) Miocene sedimentary biodetrital rock. It is light cream with a delicate, grained textured surface. It is formed of crushed reef carbonate fragments deposited together with small amounts of binding material. Calcite skeletons are cemented with the crystalline calcite. Haber et al. (1988) identified two main types of Pińczów limestone, a coarse-grained variety, which is durable and a fine-grained, which decays easily. The durability of Pińczów limestone is strongly related to its texture.

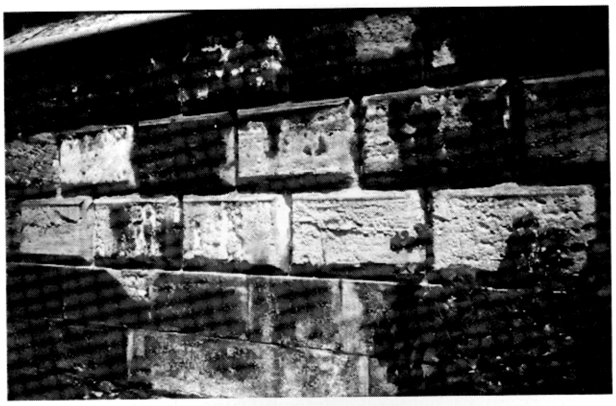

Figure 4.12 An alveolar pattern underneath a thin gypsum crust. Libiaż dolomite. The walls surrounding Wawel Cathedral.

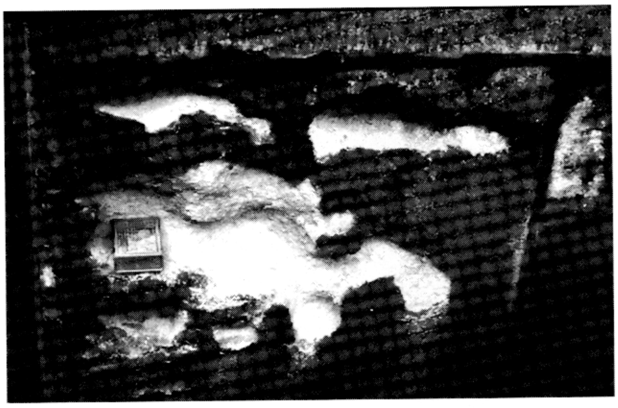

Figure 4.13 Honeycomb weathering of the front façade of the Church of Saints Peter and Paul. Libiaż dolomite.

Carpathian flysch sandstone, used for the preparation of the bases of the sculptures of the apostles, is described here as an example of the weathering of these rocks. Carpathian flysch sandstone was frequently used as a building material in Kraków architecture. This sandstone, which occurs in all structures in the Carpathians, is much varied, with a broad spectrum of properties (various grain size, framework grain composition, matrix content, cement content and composition, porosity, etc.). The weathered sandstone investigated here is creamy to yellowish due to admixture of iron oxides, medium-grained to coarse-grained, and contains carbonate cement.

4.4 DAMAGES ON THE STONE MATERIAL

4.4.1 Weathering of Libiaż dolomite

The Libiaz dolomite in the historical architecture in Kraków has decayed rapidly during the last fifty years. On the wall surrounding the Wawel Cathedral, the portal of the external gate of the Royal Sarcophagus and the front façade of the Church of Saints Peter and Paul, were 1-30 cm^2 alveolar cavities from 1-4 cm deep (Figures 4.12, 4.13).

The damaged rock surfaces were carefully examined. The cavities were soft, crumbly and scaly. Assemblages of magnesium sulphate hexahydride, epsomite (i.e. magnesium sulphate heptahydride) and gypsum (calcium sulphate dihydride) occurred as 100-500 μm thick discontinuous encrustation. Considerable amounts of salts were concentrated at the bottom of the gradually eroded cavities, where they were protected against washing rain. Part of the exterior surface of the dolomite stone was covered with a dark crust of minute needle-like gypsum crystals including large amounts of up to 60 μm large dusts particles.

Cavernous and honeycomb weathering (alveolar patterns) was characteristic of the surfaces exposed to rain and wind action. The porosity (7% to 12%) and imbibition (2.3% to 5.6%) of the dolomite permits moderate to good moisture penetration. The movement of ions from the rock dissolved by rainwater towards the stone surface and ions from rainwater into the rock, and cementation of pores by precipitated and crystallized soluble salts, fundamentally alter the properties of the surface layer of the stone compared with those at depth. This is probably the main reason of alveolar pattern development. As wind speeds up the evaportation of water the soluble salts crystallises.

The deterioration of the dolomite (Figure 4.15a) is caused both by dusts and gases. The amount of calcium and magnesium bicarbonate dissolved by rainwater depends mainly on the water temperature and the partial pressure of CO_2 in the air, as calcium bicarbonate is about a hundred times more soluble than calcium carbonate, 1.1 and 0.014 g/l respectively (Amoroso & Fassina, 1983).

Sulphates crystals grow both inside cavities and on the external surfaces as stone components react with sulphur dioxide in atmosphere in the presence of carbon particles. Rainwater evaporation after rainfall is also a possible source of gypsum crystallisation. Gypsum crystallises in the form of elongated crystals (Figure 4.14) of magnesium sulphate hexahydride and epsomite (magnesium sulphate heptahydride) and causes the disruptionof the dolomite by mechanical force. Hexahydride and epsomite takes up and loses water relatively easily in response to changes in temperature and humidity. Because of the hydroscopic nature of these salts, dolomite absorbs more moisture from the atmosphere especially after their crystallisation inside pores, and make the stone more susceptible to frost weathering. Variation in volume between sulphates and the dolomite they replace as well as different thermal expansion between gypsum and dolomite accelerates stress and cracks the dolomite.

4.4.2 Weathering of Upper Jurassic limestone

The Jurassic limestone in Wawel's fortification walls from the 19th century, have contrasting black and white zones (Figure 4.16). The white zones develop on surfaces exposed to rains, which washes out airborne pollutants and initiates formation of a crust of gypsum on the surface. The gypsum crust is not stable; solutions migrate freely into the limestone. Here the gypsum repeatedly dissolves and recrystallises in the alternating episodes of wetness and dryness of the stone, and causes mechanical stresses in pores and cracks.

The intensive blackening was typical of humid surfaces exposed to the north. Also here gypsum crust forms. The surface of a black gypsum crust is uneven, from 0.3 to 10 mm thick, with subparallel folds or mushroom-shaped forms. Polarising microscopes and scanning electron microscope pictures show that the darkening is caused by black fly ash particles (Figure 4.17), but it probably also comes from microorganisms, such as cyanobacteria. Their role in weathering of limestone surfaces, often re-

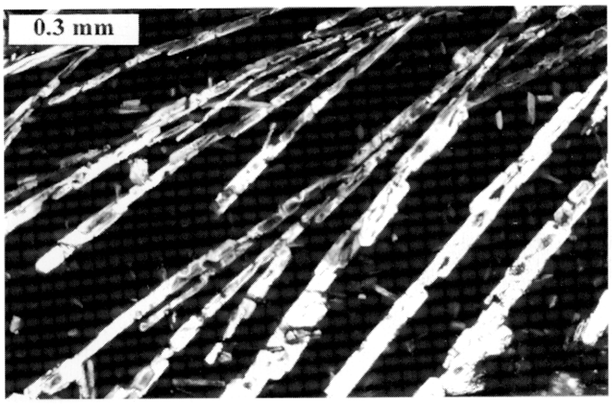

Figure 4.14 The crystal habit of gypsum crystallises from precipitation in Kraków. Optical microscope observation, crossed polars.

sulting in a black surface, was noted by e.g by Viles, 1995, and Wakefield & Jones, 1998.

Gypsum crystals in the form of needles and rosettes are frequently found on the black surface, as well as inside in fissures, veinlets and nests. A weakened zone develops at the boundary between pure limestone and the gypsum-containing layers. Calcite was found to dissolve selectively, and reprecipitate in a 100-200 μm thick layer of minute calcite crystals. Gypsum dissolves 25 times more easily than calcite (Winkler, 1994) and its solubility increases in the presence of many different salts (Goudie & Viles, 1997).

Limestone covered by a black gypsum crust suffers more serious damage than washout by rain. The presence of gypsum or sometimes other salts generate stress by three mechanisms.

Firstly, the black gypsum crust absorbs more solar radiation than the white surface. The linear coefficient of the thermal expansion of gypsum is about five times that of calcite (Goudie & Viles, 1997). Disruptive thermal gradients between the subsurface and surface can lead to exfoliation development during repeated heating-cooling cycles (Figure 4.18).

Secondly, salt weathering of the limestone is recognised as one of the primary factors of deterioration. Blistering and exfoliation of a few millimetres thick gypsum crusts is the main reason for the decay.

Thirdly, the moisture facilitates microorganism growth. Microorganism, bacteria, algae and fungi, located on rocks in the city are less frequent than in rural areas, probably limited by rapid salt precipitation, but still found. In winter sulphur oxidising bacteria (*Thiobacillus thioparus, Th. thiooxidans, and Th. denitrificans*), producing sulphuric acid, dominate, and in summer nitrifying bacteria (*Nitrobacter, Nitrococcus, Nitrosomans*), oxidising nitrite, are more common. Also cyanobacteria (blue-green algae) chemically attacks calcite crystals and dissolve calcite, producing micro-scale boreholes and pitting. (Figure 4.15b).

4.4.3 Weathering of Pinczów limestone

The sculptures in of the Apostles from the 18th century, made in Pinczów limestone, were badly blackened and in an advanced stage of decay (Figure 4.8). Some of the badly disintegrated carved elements could not be recognised, and material and stone fragments from surface and subsurface layers of the Pinczów limestone had crumbled. Gypsum crystals had formed under the surfaces layers of the lime-

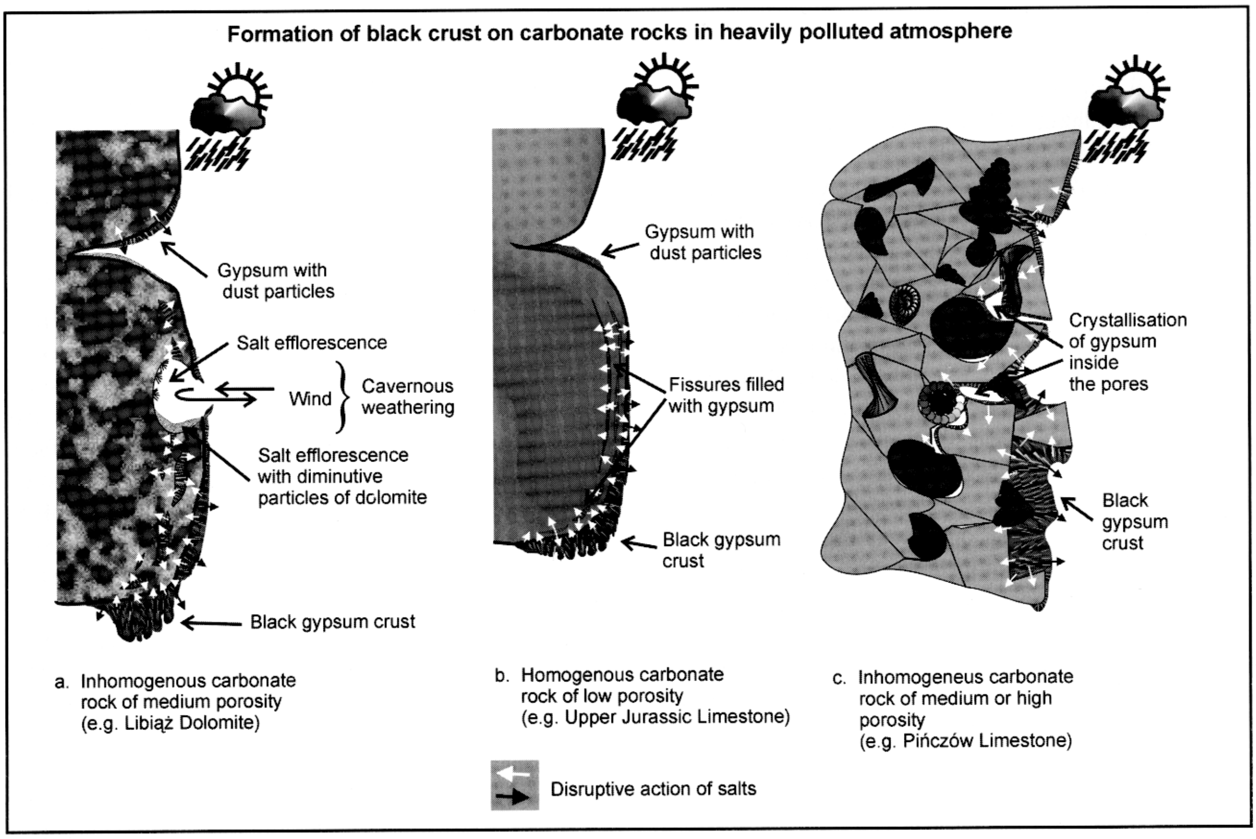

Figure 4.15 Formation of black crust on carbonate rocks in a heavily polluted atmosphere: a) Inhomogenous carbonate rock of medium porosity, b) Homogenous carbonate rock of low porosity, c) Inhomogenous carbonate rock of medium or high porosity.

Figure 4.16 Strongly contrasted white (exposed to running rainwater) and dark (protected from direct rainfall) surfaces. The Upper Jurassic limestone. 19th century Wawel fortification.

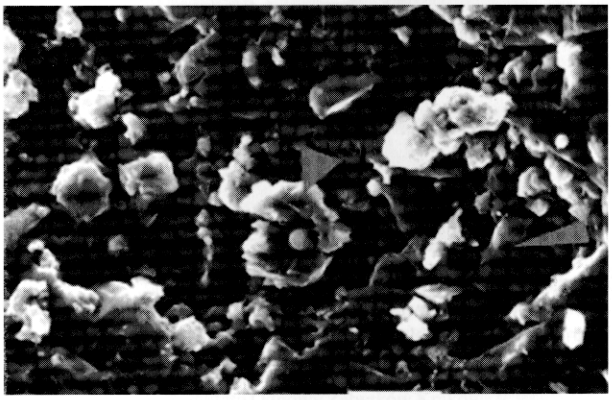

Figure 4.17 Spherical particle of aluminosilicates inside the rosette of plate gypsum crystals on a Jurassic limestone surface. 19th century Wawel fortification.

stone, as rainwater penetrates through the pores deeply into the stone.

Newly formed gypsum is easy to remove from pores of bigger size. Fine-crystalline gypsum has filled the small pores of the rock. The crystallisation of gypsum causes mechnical stresses in small and medium-sized pores and cracks. The deterioration mechanisms are typical for medium porous to high porous carbonate rock (Figure 4.15c).

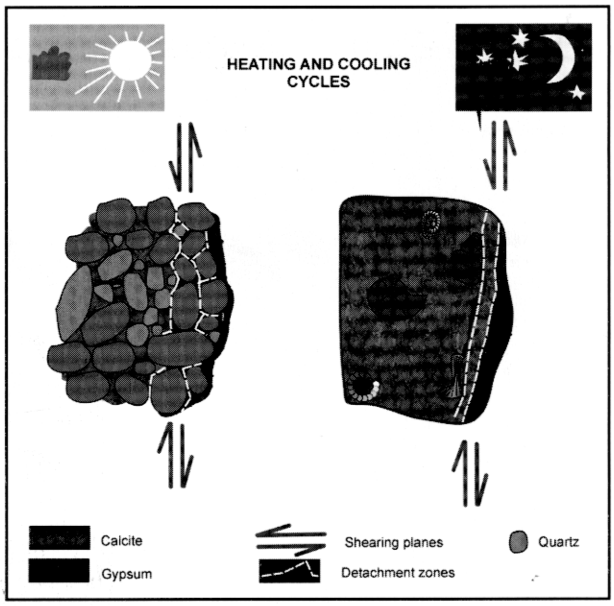

Figure 4.18 The mechanism of weathering of rocks due to heating-cooling cycles.

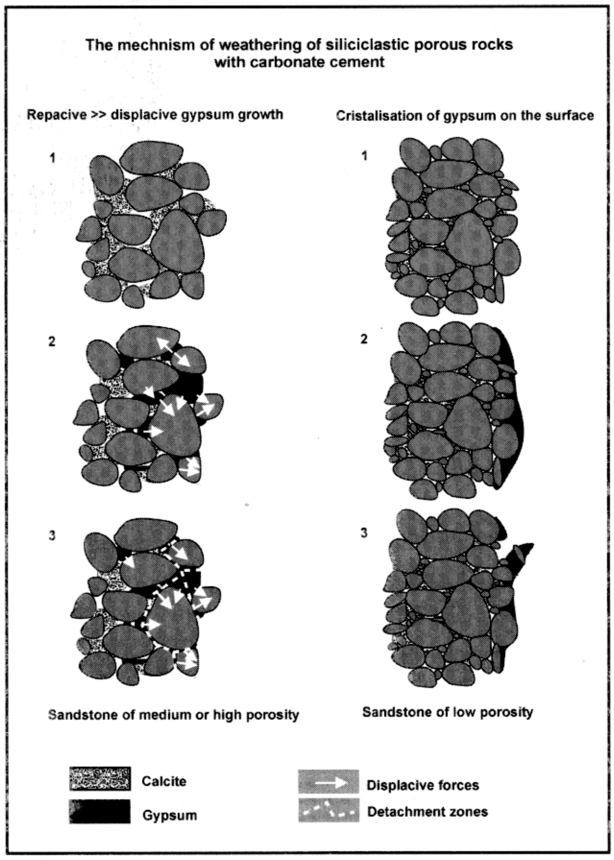

Figure 4.19 The mechanisms of weathering of siliciclastic porous rocks with carbonate cement.

4.4.4 Weathering of Carpathian flysch sandstone

The statues of the Apostles were placed on bases carved in Carpathian flysch sandstone. Because of its sensitivity to pollution these old sandstone bases experienced severe decay. In sandstones containing carbonate cement, which was the material of the original bases, destruction occurs because the volume of primary cements is reduced and dissolved by precipitation water. Then the carbonate is replaced by gypsum (Figure 4.19). Gypsum fills also empty voids in the rock. All these processes result in the weakening and accelerated decay of the structure of the rock.

The final stage of the process is the formation of gypsum cemented sandstone. This has a "float texture", in which detrital quartz grains are dispersed in gypsum cement. The structure of the rock is weakened not only by exchange of cement but also by mechanical displacement forces induced by the growing gypsum, especially distructive in highly porous sandstones (containing or devoid of carbonates).

The later stages of weathering of the bases described here, has been manifested as disintegration, exfoliation, crumbling, and rounding of edges (Figure 4.20). Together with the detached gypsum crust some components of sandstone are removed from the rock surface.

Figure 4.20 The later stages of weathering of old sandstone bases, manifested as disintegration, exfoliation, crumbling, and rounding of edges. Church of Saints Peter and Paul.
Photo: Wanda Wilczynska-Michalik.

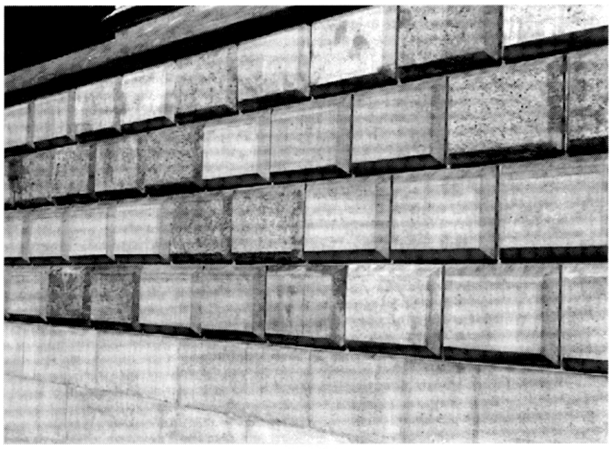

Figure 6.21 The walls surrounding Wawel Cathedral after renovation. Photo: Wanda Wilczynska-Michalik.

Figure 4.22 The façade of the Church of Saints Peter and Paul after renovation. New copies of the statues of the Apostles carved in the 1980s. The blackening of surfaces. Pińczów limestone. Photo: Wanda Wilczynska-Michalik.

4.5 CONSERVATION

4.5.1 Conservation projects

The deterioration of stones in exposed sculptures and buildings has been evident for many concerned observers throughout the centuries.

Renovation works undertaken since the beginning of the 20th century included refitted roofs and domes, elevation preservation, stone and brick elements restoration, endangered stone-work and architectural details both in the interior as well the exterior.

Extensive conservation works in Kraków began at the end of the 1970's. For the last ten years conservation work has been carried out according to a complex plan prepared by the Cracow Monuments Renovation Social Committee.

Since 1992 the majority of all renovation work within the city centre have been finaced by the National Fund (Krasnowolski, 1999). Other sources of funding has been the Kraków Governor, the City of Kraków Commune and private donors. A total of 40,4 million PLN (10,5 million Euro) was spent for renovation and conservation works in 2000 (Krasnowolski, 2001). A further phase of renovation work is prepared.

4.5.2 Results of restoration work

Conservation treatments of the building stone has included cleaning by physical removal of weathered crusts and soluble salts, consolidation of stone that has lost cohesion, impregnation of the weathered stone, as well as a substantial part of the underlying sound layer of the stone.

The Libiąż dolomite on the wall surrounding the Wawel Cathedral, the portal of the external gate of the Royal Sarcophagus and the front façade of the Church of Saints Peter and Paul have now been restored to their unweathered appearance. The 18th century sculptures of the Apostles that decorate the fence in front of the Saints Peter and Paul church, which were heavily decayed, were replaced by copies in the 1980s. After about twenty years of exposure, blackening of the surfaces can be noticed on the new statues (Figure 4.22).

The bases of the sculptures, made in Carpathian flysch sandstone which is especially sensitivity to pollution, were badly damaged. New bases, made in a different type of sandstone, replaced the original ones in 1980s. The copies of the statues of the Apostles, which are now on view, are placed on these new bases.The Cathedral has through these measures regained much of its former magnificence.

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