MODELLING OF THE NATURAL STONES DEGRADATION IN POLLUTED ATMOSPHERE

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Abstract

This paper describes the effect of air pollutants on Portland limestone and mathematical models of its degradation in form of dose-response function evaluated as the result of exposure in different areas of Europe. The dose-response function was used to calculate stone damage in the area of selected cities in Poland. Based on examinations carried out in Cracow equations being used for an evaluation of soiling of the limestone surface with particulate matter ere appointed.

Streszczenie

Przedstawiono wpływ zanieczyszczeń powietrza na wapień portlandzki i matematyczne modele jego degradacji w postaci funkcji dawka-odpowiedź będących wynikiem ekspozycji na różnych obszarach w Europie. Funkcje te zostały zastosowane do oceny przewidywanych zniszczeń na obszarze kilku miast w Polsce. Na podstawie badań w Krakowie wyznaczono także równania służące do oceny zabrudzenia powierzchni wapieni pyłem zawieszonym.

Keywords: **Stone; Pollution; Sulfur dioxide; Soiling; Dose-response function.**

1. INTRODUCTION

Stone was one of the first building materials used by man and it is still in use today fulfilling the same function as a structural material for buildings, for utilitarian articles, objects of worship and ornaments. The stone as the conglomeration of chemical compounds is subject to chemical reactions with the surrounding environment and physical-mechanical and microbiological processes as a function of the reactivity of the minerals and the aggressiveness of the environment.

A very severe indication of the impact of the environment on stone are badly weathered sculptures on the front of the church of St. Peter and Paul in Cracow that have been affected of aggressive pollutants emitted by industry, as well as become soiled and covered with lichens.

2. CHARACTERISTICS OF LIMESTONE

2.1. Chemical composition and structure

Among historical and contemporary structural materials stones coming from sedimentary rocks have a dominating position on account of the ease of processing and their ability to provide a decorative finish. But many of them are sensitive to the impact of the environment, especially in polluted urban and industrial atmospheres. Limestone is a sedimentary rock formed mainly of calcium carbonate ($CaCO_3$) with different crystallographic structures [1,2].

The main components of limestone comprised calcite and matrix of micrite or sparite as well as additives which can contain aragonite, dolomite, siderite, quartz, pyrite, clay minerals, and remains of organ-

isms. The main component of limestone, calcite, is a mineral formed primarily of calcium carbonate. It is brittle, clear, and often contains a mixture of additives of manganese, iron and magnesium. Micrite and sparite are also calcium carbonate but with significantly smaller crystals [1,2].

Properties of limestone depend on the nature of organic residues from which the rock was formed, the chemical processes during their creation, the type of products of these reactions, and accompanying physical and geological processes. Limestones with mineral or clayey cement have a different performance depending on the type of the filling, with the more long-lasting ones having crystalline cement characterized by a low porosity and low water absorption.

Limestones formed of carbonate minerals are white, but quite often stones show a diverse range of colors resulting from impurities.

2.2. Effect of environment on the durability of limestone

All stones are porous materials, with the solid phase differing in the structure and the ratio of density (crystal of minerals) and porosity us (intergranular spaces and additives). There are three types of pores which behave in the different way during the absorption of water and other solutions [1,2]:

– closed pores remain intact and do not affect the weathering process,

– open pores which fill with liquid in normal conditions,

– micropores which can be filled only in forced conditions (e.g. under the increased pressure).

The durability of natural stone is closely linked to the chemical composition of the mineral present, but is also strongly descended on the porosity and pore structure.

Chemical reactions between the impurities from the atmosphere and components of the stone can occur not only on the surface of the material, but also on the surface of the pores, so the larger the open porosity the greater contact area and reduction durability of the material. Other basic physical properties indicating the durability of the stones include density, density ratio (defined as the ratio of the volume of water absorbed at normal pressure to a volume of water absorbed in the total pore volume of space available for water (often known as the Hirschwald co-efficient).

Symptoms of the damage depend on the type of exposure, its intensity, and the length of the exposure.

Among the gaseous air pollutants with a greatest influence on the degradation of stones are sulfur dioxide and nitrogen oxides (NO_x). In the presence of catalysts, they are oxidized into acids and are deposited in the form of acid rain, fog or condensation and these are the main causes of chemical weathering [2-4].

Chemical processes in the polluted air are leading to the dissolution of mineral crystals, leaching soluble products or the formation of deposits of greater volume that can lead to splitting, cracking and surface loss. Products of these reactions, especially the chlorides and nitrates can move deep into the stone and crystallize there in the form of hydrated salts with a greater volume than calcium carbonate [2-4].

Water can come from rain, snow, vapor or mist but also water penetrating the stone by the capillary action from the ground.

In the case of limestone, crystalline calcium carbonate, for example marble, the change to an amorphous form can be shown by a loss of gloss. This effect is long-lasting but carbonic acid penetrating into the deeper cracks can be more serious as it damages the structure of the rock. Salts contained in the rain or capillary structure are particularly damaging for stones with a high absorption of water in the form of damage depending on the type of salt present. Sodium chloride crystallizing in the pores of the stone increases the volume and causes cracking. Sodium sulphate (Na_2SO_4) forms fibrous minerals that cover the surface, calcium and potassium sulphate (K_2SO_4) form a hard dense crust. The intensity of these processes depends on the climatic conditions, temperature and humidity. Ammonium salts cause the decomposition of calcium carbonate with the creation of the more soluble calcium chloride ($CaCl_2$), which is also highly hygroscopic and takes a large amounts of water increasing the volume repeatedly.

Crystallization and the dissolution processes of the salts may occur periodically with the change of climatic conditions and this intensifies the degree of destruction as the solutions penetrate more deeply into the cracks in the rock. Temperature changes also have a damaging effect on porous stones structures [5].

Micro-organisms and tiny flora can also be an important factor. These organisms produce a variety of metabolism products, interact with each other, and

react with the substrate and the environment.

Among the bacteria a major role is played one that is sulfate producing or nitrifying. Sandstones and limestones are particularly at risk. The product of the metabolism of sulfate bacteria is sulfuric acid which dissolves the calcium carbonate to form calcium sulfate ($CaSO_4$) (gypsum) with a higher specific volume. Fractures are formed in the pores and on the surface growths (crusts) are formed [2,7].

The metabolic product of the nitrifying bacteria is nitric acid, which on reaction with calcium carbonate formed nitrates that are readily soluble in water, and which are either washed out by rain or during the dry periods form characteristic white spots ("know patches") or yellow dust deposits.

Suspended particles (both solids and liquids) covering the surface of the stones can react with them or with the contaminants already present to form new products [2-6].

Dust not only degrades stones, but also spoils the aesthetic experience of often beautiful and valuable objects.

The degree of stone degradation depends not only on the aggressiveness of the environment but also on the exposure conditions. In conditions where there is direct action of gaseous pollutants and rainfall a loss of material is observed but in the case of the exposure in locations sheltered from rain, there is an increase in weight and in linear dimensions.

The particular aggressiveness of the urban environment results from enhanced effect of sulfur dioxide (SO_2) and dust heightened with presence of nitrogen oxides (NO_x) and high concentrations of ozone (O_3). Such situations are being observed, for example, in big cities in southern Europe where in street canyons a peculiar mixture of the substances contained in the exhaust fumes is created [8,9].

 However, in the northern European countries with low SO_2 concentrations the greater impact on the loss of material is due to rainfall and low temperatures.

3. THE RESULTS OF STUDIES OF PORTLAND LIMESTONE EXPOSED ON MONITORING STATIONS IN POLAND AND OTHER EUROPEAN COUNTRIES

3.1. The test conditions

Preparation of the samples

Studies of Portland limestone have been ongoing since 1987 at several stations in European cities as a part of the research program of the International Cooperative Programme on the Transboundary Effects of Air Pollution on Materials (ICP Materials) to the United Nations Economic Commission for Europe (UNECE). So far, measurements have been made in: 1987-1991, 1997-1998, 2002-2003, 2005-2006, 2008-2009, 2011-2012 [11-17]. Since 2000 exposures have also be organized in Katowice and Krakow on corrosion testing stations of the Institute of Precision Mechanics located at pollution monitoring stations.

Portland limestone is an oolitic limestone from the Portland Beds of Upper Jurassic age (136-160 million years ago). The quarries are located on the Isle of Portland in Dorset, England. The tablets used in the exposure programme were obtained from the Whit Bed at Fancy Beach Quarry. The stone is a buff colored shelly stone and petrographic study shows the stone comprises ooliths and shell fragments surrounded by calcite cement. The inter-granular porosity is between 22 and 23%. The limestone samples were prepared in the laboratory of Building Establishment Research Ltd.

The stone tablets were sawn from blocks into tablets; 50 × 50 × 8 mm (±2 mm) in dimension. A 4 mm hole was drilled at the centre of the 50 × 50 mm dimension to allow fixing to a plastic support (carousel). Stone dust was removed by brushing with a nylon brush under running de-ionised water. The tablets were air dried for 2-3 hours before oven drying at 60°C for 3 hours and then 105°C overnight (16 hours). After the tablets had cooled they were weighed and sealed in plastic bags.

The stone tablets were fixed vertically to the arms of carousels (12 tablets per carousel) that were free to rotate about a vertical axis in order to eliminate directional effects. The carousels were exposed completely unsheltered, thus receiving all weather conditions, or sheltered in a ventilated aluminium box which prevented rainfall. A number of tablets, prepared as above, were not exposed but retained as pristine (control) samples.
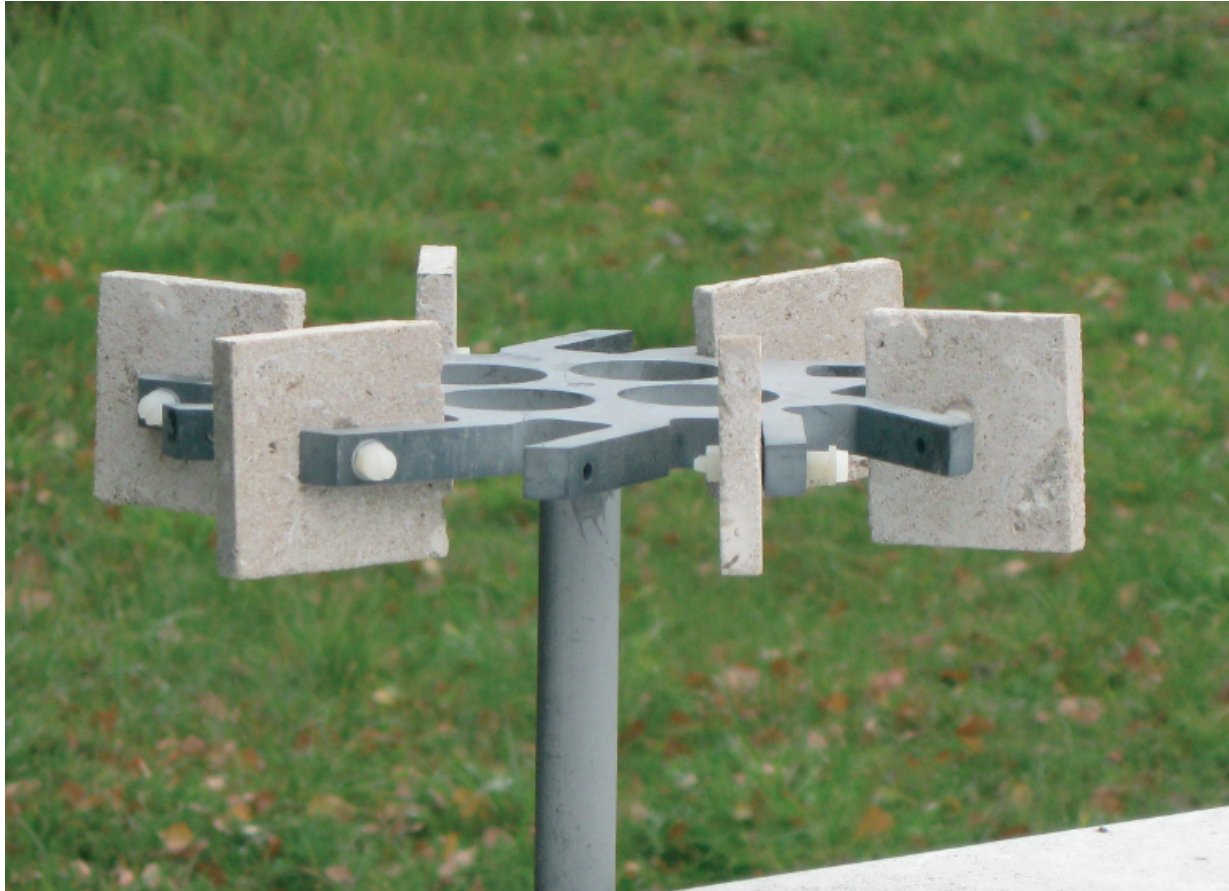
Figure 1.
Carousel with stone samples

Stones were exposed in unsheltered and sheltered conditions for periods of 1 year, 2 years and 4 years.

At the end of the exposure period the tablets were oven dried as before and re-weighed. Weight changes have been converted to recession rates in μm [12]. To evaluate changes in the color were used measurements of reflectance using a reflectometer SHEEN Opac 310, the optical configuration is set by the geometry 45°/0° according to ISO 6504 , ASTM E97 and DIN 55984.

Atmosphere condition

The environmental conditions measured at all the exposure sites included temperature, relative humidity, sun radiation, SO_2, NO_2 and O_3 by and annual rainfall [10] The rainfall was analysed for pH, conductivity and soluble salts: Cl^-, SO_4^{2-}, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}.

In most of the countries atmospheric concentrations of less than 15 μg/m^3 SO_2 has been measured during

the four years of this programme, but there are some higher readings in the Czech Republic, at one of the German sites and the highest reading of all, in Poland. In most of the big cities an average yearly NO_2 concentration was below 40 μg/m^3. The average level of O_3 was between 30 and 60 μg/m^3 but there were a few sites where the level was much lower, for example just 15 μg/m^3 at the site in Portugal, and much higher, for example 86 μg/m^3 at site in Spain.

3.2. Analysis of the exposition result

After analysis following one year, two years and four years exposure it is clear that there is a higher surface loss shown by the recession rates amongst the unsheltered samples.

On the whole the surface loss on the majority of samples was greater after exposure for two years than after one year and is greater still after four years [13,14].

On the base of the results of investigations carried

out in 1987-1988, Pearson correlation coefficients between selected environmental factors and linear corrosion losses after one-year of exposure on 34 corrosion sites were determined. Ranking effect is as follows: SO_2> pH precipitation> rainfall> Cl^- in precipitation> SO_4^{2-} in precipitation. Fig. 2 shows the linear corrosion losses of limestone during the annual exposure in selected urban corrosion sites in Europe in 1987 and 2012 and the annual average SO_2 concentration.
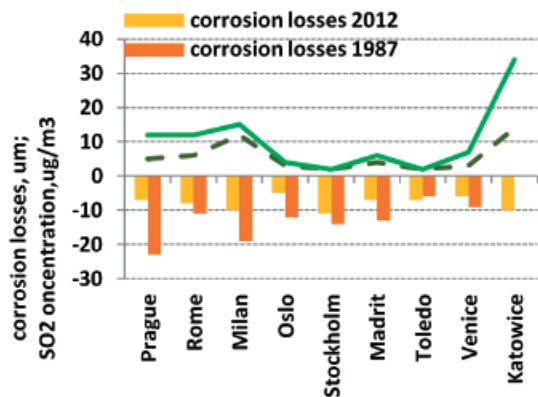

Figure 2.
Average annual losses of Portland limestone and the concentration of sulfur dioxide in 1987 and 2012 in European cities (on the basis of [13-17])

The exception to the dominant influence of SO_2 is the station in Stockholm, where a high rate of weathering can be attributed to other factors such as chlorides and of the total precipitation.

3.3. Model of annual loss of Portland limestone

A literature search for data of investigation of stones in natural conditions results in a number of dose-response function particularly limestones and marbles. Data are summarized in Table 1.

Table1 contains corrosion losses calculated for corrosion station in Katowice with use account to atmospheric conditions in 2012 year.

Exposure in Europe in period 1987-1991 in ICP Materials Programme enabled the formulation of the empirical relationship between corrosion hazard and corrosion losses of limestone in form (R5). The predicted values have been plotted against the actual results exposure but the correlation seems to be poor.

Results of European exposure carried out in 2001-2004 in conditions where SO_2 concentration decreasing rapidly on corrosion sites involved in the program confirmed the impact of SO_2 on the stones degradation but an increase in the effect of NO_2 and dust especially in the cities was observed.

The equation describing the relationship between air pollution parameters and corrosion losses in the new environmental situation is (R6):

$$R = 3.95 + 0.0059[SO_2]RH_{60} + 0.054 Rain[H^+] + 0.078[HNO_3]RH_{60} + 0.0258PM_{10} \qquad (1)$$

HNO_3 concentration can be calculated from the relationship:

Table 1.
Dose-response function for limestone [12,14,16]

No	Dose-response function	Corrosion losses calculated for Katowice , µm	Ref.
R1	R (µm per m of rain)= 25.7+0.10[SO_2]	36.4	[12]
R2	R (µm per m of rain)= 12.5+0.054[SO_2]	17.7	[12]
R3	R (µm per m of rain)= 8.5+0.020[SO_2]	11.7	[12]
R4	R (µm per m of rain)=7.6+0.30[SO_2]	15.7	[12]
R5	R = 2.7 [SO_2] 0.48 exp - 0.018T) + 0.019Rain [H^+]	5.9	[14]
R6	R = 3.95 0.0059 [SO_2] 0.054 RH_{60} Rain[H^+] 0.078 [HNO_3] RH_{60} 0.0258 PM_{10}	8.3	[16]

where: R – corrosion losses,µm; [SO_2] – SO_2 concentration, µg/m³; T – temperature, °C; Rain – sum of precipitation, mm; [H^+] – concentration of H^+ ion, µg/m³, [HNO_3] – concentration of nitric acid, µg/m³, RH_{60} – relative humidity over 60%, %, PM_{10} – concentration of dust PM_{10}, µg/m³

$$[HNO_3] = 516exp-3400/(T +273)\{[NO_2] [O_3] RH\}^{0.5} \tag{2}$$

where: $[NO_2]$ – NO_2 concentration, $\mu g/m^3$; $[O_3]$ – ozone concentration, $\mu g/m^3$; RH – relative humidity, %, T – temperature, °C.

The use of equations (R1-R4) for conditions on the site in Katowice results in high erosion losses, exceeding 2 up to 6 times losses expected from equations (R5) and (R6). The use of equations (R5) and (R6) for the environment conditions of some cities in Poland gives probable erosion losses shown in Figure 3.
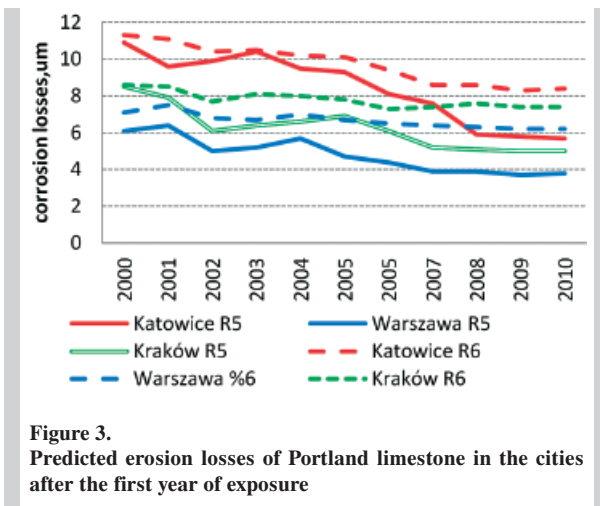

Figure 3.
Predicted erosion losses of Portland limestone in the cities after the first year of exposure

Corrosion losses determined from equation (R6) are higher than from equation (R5) because the impact of traffic pollutants is included: nitrogen oxides, ozone and particulate matter.

4. DEGRADATION OF PORTLAND LIME-STONE DURING LONG-TERM EXPO-SURE

With a relatively constant intensity of environmental hazards the magnitude of erosion losses is roughly proportional to the duration of exposure. Table 2 shows the parameters of the equations describing the dependence of linear losses of limestone in the form:

$$C = At^n \tag{3}$$

where C – the magnitude of change over time t, μm

A – corrosion losses after the first year of exposure, μm

n – coefficient characterizing the intensity of environmental action,

t – time, number of years

With decreasing levels of air pollution, a decrease of the rate of degradation characterized by a factor n is observed. In the period of 10 years the annual linear losses of Portland limestone reduced on average twice, slightly less in areas with low levels of pollutants contamination. At that time, the concentration of sulfur dioxide in industrial and urban areas dropped more than 3 times , but at the same time cities had increased significantly the concentration of nitrogen oxides and dust so that the rate of corrosion damage observed in the period 1998-2001 stopped.

5. MODELLING THE IMPACT OF DUST ON DEGRADATION OF THE APPEARANCE OF OBJECTS MADE FROM PORTLAND LIMESTONE

Presence in the air of high concentration of dust results not only in material degradation, but also a decrease in the aesthetic appearance. The walls of buildings located along routes with heavy traffic are becoming soiled, particularly the first 2-4 floors. In cities where high buildings form canyons gases and dust move not only with the direction of the wind but also in response to the forces caused by turbulence caused ahead of the vehicles and by planning arrangement of buildings. Vortices are formed and at the same time the reactions between the emitted NO, NOx, ozone, and radicals, and the solar radiation are

Table 2.
Rates of progress of Portland limestone damage during exposure in different conditions (own study on the base [6])

Type of environment	Exposed in 1988-1991			Exposed in 1998-2001		
	n	A μm	SO_2 concentration, $\mu g/m^3$	n	A μm	SO_2 concentration, $\mu g/m^3$
Industrial	1.23	9.0-22.0	34.2	1.02	6.0-11.7	17.5
Urban	0.68	8.0-12.5	18.3	0.96	2.0-10.5	8.0
Rural	0.50	6.0-14.8	4.5	0.50	4.5-8.9	2.1

occurring. Distribution of pollutants concentration inside the vortex depends on the ratio of the height of buildings to the width of the road and the wind direction above the canyon. Numerous models of different scale applications are used to describe this phenomenon [16].

The degree of change of surface cleanliness (measured as the degree of light reflection from the surface towards the white pattern) of white Portland limestone exhibited in various places in Krakow in Fig. 4 has been demonstrated. Samples were situated vertically under the cover protecting against rain [8].
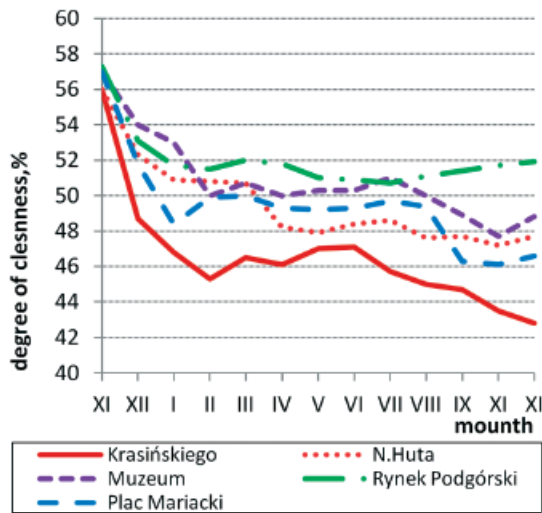

Figure 4.
Degree of cleanness, % sample surface of white Portland limestone exposed in different places in Krakow (own unpublished results from the author's research)

The equation describing the change of limestone surface covering by dust in the function of time is as follows:

$$\Delta R = R_o [1-\exp (-C_{PM10} \cdot 3.10^{-6} t)] \qquad (4)$$

where: ΔR – change of the surface cleanliness,%; R_o – cleanliness at time 0,%; t – time of exposition, days; C_{PM10} - PM$_{10}$ concentration, $\mu g/m^3$

Based on these observations it is possible to evaluate the degree of surface covering by dust depending on its concentration in the selected time.

The result of the calculation in the case of white Portland limestone is presented in Fig. 5.

On the bright surfaces a loss of cleanness approximately 35% is visible. If we accept this value as a level for surface washing, at small concentration of partic-

ulate matter (30 $\mu g/m^3$) predict period of time between cleaning will occur about 13 years, but at high concentration (80 $\mu g/m^3$) about 5 years.
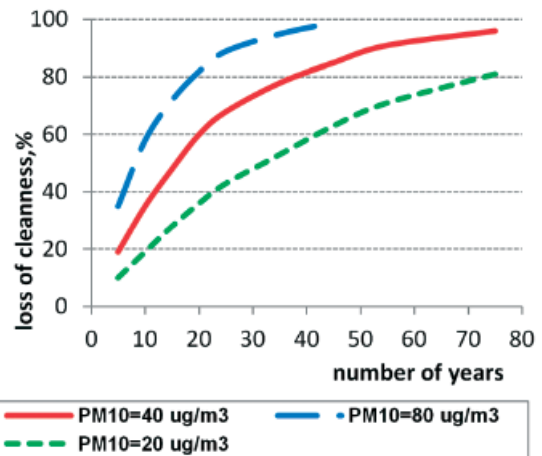

Figure 5.
Area of white limestone covered by dust as a function of the concentration of particulate matter and time (own study based on unpublished results of the author)

It should be noted that equation relates to the covered surfaces. The rainfall will undoubtedly change the level of contamination and the form of equations [10].

6. SUMMARY

Presented equations, particularly those determined in recent years, can be applied and allow to determine the damage of limestone in a selected area. Using spatial visualization software it is possible to create of damage maps. Due to high level of NO$_2$ concentration on some area in Katowice and Krakow corrosion losses of Portland limestone decrease slowly.

However, it is possible to prevent damage through activity aimed at the significantly reduction of pollutants emitted to the atmosphere.

Accepting the ccurrent air quality standard of annual average PM$_{10}$ concentration 40 $\mu g/m^3$, based on protection against adverse health effects, for critical level for limestone visible effects can be observed after about 10-12 years.

Further studies with improved time resolution for data collection and longer exposure periods, probably up to at least 10 years, are required for this scientific justification.

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