

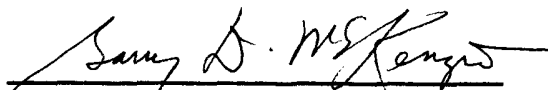
Senior Thesis

The Effect of Acid Rain on Natural
Stone Buildings and Monuments

by
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Approved by:

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INTRODUCTION

During the past twenty-five years, acid rain has been one of the most widely publicized environmental issues. Most recent studies of the effects of acid rain concentrate on ecological and environmental impacts. This paper reviews the effects of acid precipitation on natural stone buildings and monuments and discusses possible methods of protection and preservation of the exposed structures. A brief introduction to various aspects of the acid rain phenomena (including 1) sources of the major acid-forming compounds, 2) transformation and transportation of these compounds, and 3) their deposition) provides important background information on this geographically widespread problem.

GENERAL INFORMATION ON ACID RAIN

Scientists were aware of the fact that the chemical composition of precipitation varied as a result of the scavenging of atmospheric gases and particles. Detailed studies of the chemistry of precipitation and acid rain did not begin until the 1950's when an organized monitoring system began in northern and western Europe (Bubenick, 1984). Prior to this time, the magnitude and extent of acid rain remained a mystery. The acid rain problem of the northeastern United States and Canada was not recognized until the early 1970's (Bubenick, 1984). Once recognized as a serious problem, extensive research revealed information on the sources, transformation and transportation, and deposition of acid forming compounds.

Sources of Acid Forming Compounds

The important contributors to rain acidity consist of carbon dioxide, CO_2 , and the oxides of sulfur, SO_x , and nitrogen, NO_x (Johnson, 1986; Likens, 1976; Winkler, 1982). These compounds react with water and other agents in the atmosphere to form carbonic, sulfuric, and nitric acids (Johnson, 1986). SO_x and NO_x are most important in forming the low pH values measured in acid rain. Bubenick, 1984, reported that 62% of rain water acidity could be attributed to sulfuric acid and 32% to nitric acid. The remainder of this paper will concentrate on those compounds which form these strong acids and their effects on stone buildings and monuments.

The sources of acidifying compounds may be grouped into two categories : natural and anthropogenic.

To determine man's influence on the acidity of precipitation, a knowledge of background levels or natural concentrations of CO_2 , SO_x , and NO_x is necessary. Natural sources of CO_2 consist mainly of the photosynthetic reactions of plants, but may include emissions from naturally occurring forest fires. Gaseous CO_2 dissolves in water to form carbonic acid. The pH of pure water in contact with atmospheric CO_2 is 5.6 (Likens, 1976). Thus, acid precipitation with a pH less than 5.6 is considered acidic (Bubenick, 1984).

Natural sources of SO_x include 1) sea spray containing sulfates, 2) volcanic eruptions, and 3) biogenic sulfur compounds originating from the decay of organic matter (Bubenick, 1984). Natural sulfur emissions are responsible for 147×10^6 metric tons of sulfur per year, which is equivalent to approximately 60% of the total global sulfur burden (Bubenick, 1984).

Oxides of nitrogen occurring naturally in the atmosphere originate from the decomposition of nitrates and from the reaction of nitrogen compounds with lightning. The natural concentration of NO_x in the atmosphere is difficult to measure as a result of its mode of formation (Bubenick, 1984).

Anthropogenic sources of SO_x and NO_x include the following : 1) fuel combustion for transportation and energy needs; 2) industrial processes, especially metal processing; and 3) incineration of solid wastes (Bricker, 1984). Fossil fuel combustion is responsible for 90% of the NO_x and SO_x emitted to the atmosphere (Johnson, 1986). It should be noted that these emissions vary seasonably with SO_x emissions highest during the winter months and NO_x emissions highest during the summer months (Bubenick, 1984). Globally, man's activities are responsible for 40% of the sulfur burden, but in regions of high industrialization, man may contribute as much as 90% of the total sulfur emitted. Such is the case in certain regions of Europe and the northeastern United States (Bubenick, 1984).

In summary, the acid forming compounds of SO_2 and NO_x have been emitted to the atmosphere since the 1900's in the northeastern United States (Johnson, 1986). Winkler, 1975, also noted the deteriorating quality of the urban atmosphere since the beginning of the industrial revolution and noted its effect on the rate of decay of natural stone buildings and monuments. These compounds effectively lower the pH of rain to the extent that it becomes acidic. Average values of the pH of precipitation affected by these compounds range from 3-5 in the northeastern United States (Likens, 1976), but pH values as low as 2.1 have been measured in

individual precipitation events in this same area (Likens and Borman, 1974). The pH of modern precipitation is therefore significantly less than the pH of pure water in contact with atmospheric CO₂. The result of this increased acidity accelerates the rate of decay of stone monuments and buildings. Estimates for the increase in rate range from a logarithmic to a double logarithmic increase (Winkler, 1982).

Transformation and Transportation of Acid Forming Compounds

Transportation of acidic pollutants is an important consideration when deterioration occurs in rural locations or when pollutants cross international boundaries. In Sweden severe acid rain precipitation is attributed to sources in England and the Ruhr Valley, sites of concentrated industrial activity (Likens and Borman, 1974). A similar situation exists between the United States and Canada. The height of release of pollutants is an important factor in determining distance transported. Man-made pollutants are injected into the atmosphere at heights ranging from a few feet (auto exhaust) (Bubenick, 1984) to heights up to 360 meters (tall stacks) (Likens and Borman, 1974). Once in the atmosphere, conversion of SO_x and NO_x to more stable particulates of sulfate and nitrate may increase their residence time in the atmosphere (Bubenick, 1984). On the average, SO₂ possesses a mean residence time of 2-4 days, allowing time for transport over distances greater than 1000 km (Likens and Borman, 1974). Wind is the major mechanism of transport of pollutants. 55% of SO₂ emissions and 75% of NO_x emissions are carried aloft to Canada and the Atlantic Ocean from their sources in the northeastern United States by prevailing wind patterns (Bricker, 1984).

The chemical transformation of SO_2 to sulfuric acid occurs in two types of reactions : 1) homogenous gas phase reactions; and 2) heterogenous gas liquid of gas solid phase reactions (Bubenick, 1984). Homogenous oxidation of SO_2 occurs when SO_2 collides with strong oxidizing radicals such as HO^\cdot , HO_2^\cdot , and $\text{CH}_3\text{O}_2^\cdot$ (Bubenick, 1984). Heterogeneous oxidation of SO_2 occurs by catalytic oxidation in water droplets by transition metals, oxidation by ozone in the liquid phase, or surface catalyzed oxidation on collision with solid particles, especially elemental carbon(soot) (Bubenick, 1984). When combined with water such as rain or cloud droplets, the sulfates formed convert to sulfuric acid.

The transformation of NO_x to nitrates consists of a series of complicated chemical reactions in which nitrogen oxides are converted between various stages of oxidation eventually becoming nitrates. Combination of these products with water forms the corrosive nitric acid(Bubenick, 1984).

Acid Deposition

Deposition of acidic compounds upon the earth's surface can be divided into two main categories : 1) wet deposition and 2) dry deposition.

Wet deposition includes those processes^s that remove gases, liquids, and solids by precipitation. This occurs in two forms : rainout, which is the incorporation of material into cloud drops that eventually fall to the earth and washout, which occurs when material below the cloud is removed by precipitation as it falls (Bubenick, 1984). The amount of SO_2 removed by the processes of wet deposition is directly proportional to the concentration of SO_2 in the atmosphere(Schnoor, 1984). On the average, wet

deposition is responsible for removing 19% on SO₂ and 19.5% of NO_x emissions in the northeastern United States (Bricker, 1984). The remainder is transported away by prevailing wind patterns and may later be deposited by wet deposition.

Processes of dry deposition include adsorption or absorption of gases by exposed surfaces, gravitational settling, and impaction of fine particles on surfaces (Bubenick, 1984; Hicks, 1984). Dry deposition occurs continually (Schnoor, 1984) and is generally responsible for less pollutant deposition than wet deposition (Hicks, 1984). The amount of dry deposition varies seasonably with greater accumulation during winter months as a result of less precipitation (Hicks, 1984).

Thus, the processes of wet and dry deposition of acidic substances results in accelerated rates of decay of natural stone buildings and monuments. A discussion of these effects and possible methods of preservation and protection of natural stone follows.

THE EFFECTS OF ACID PRECIPITATION ON NATURAL STONE BUILDINGS AND MONUMENTS

The effect of acid precipitation on natural stone buildings and monuments is a greatly accelerated rate of decay and deterioration (Winkler, 1975; 1982). Since the beginning of industrialization, accelerated decay rates have resulted in the deterioration and destruction of innumerable buildings, sculptures, and monuments (Winkler, 1975). An example is the sculpture "The Stoning of St. Stephen" located in Westphalia, Germany. The sculpture composed of calcareous sandstone could still be recognized in a photo taken in 1908, 600 years after it had been carved. By 1968, it

had been completely destroyed beyond recognition(Winkler, 1982). In 1938, a photo of a section of frieze(a decorative horizontal band composed of marble) located on the Parthenon was compared to a plaster cast of the same section made in 1802. The cast showed only minor damage in the first 2240 years of the frieze's existence, whereas the photo was nearly unrecognizable(Yocom, 1979). Yocom, 1979, cited the intervening 136 years of industrialization and rapid increases in population as causes of the deterioration. Numerous other examples exist, all having the same principle cause : accelerated deterioration as a result of the deposition of acidic pollutants released through industrial processes.

The most pronounced decay occurs in urban areas of concentrated industrial activity or directly downwind of such areas. An examination of the urban atmosphere reveals the reason for the accelerated decay. Urban atmospheres contain three times as much sulfate as rural areas(Winkler, 1975). As noted earlier, sulfate i.e. sulfuric acid is the major contributor to rain water acidity(Bubenick, 1984). By itself, the high concentration of sulfate presents some problems, but when combined with the 10% higher average temperatures and 30 to 100% higher fog frequencies measured within urban atmospheres(Winkler, 1975), decay by sulfuric acid precipitation occurs at alarming rates.

Mechanisms by Which Air Pollutants Damage Stone

The common natural building stones consist of marble, limestone, sandstone, basalt, and granite. Those composed of calcite, marble and limestone, or cemented by calcite, calcareous sandstones are most susceptible to acid rain attack(Gauri, 1978). Silicate minerals react at a slower rate but none-the-less are affected

(Gauri, 1978). Most studies have concentrated on calcite bearing stone as they show much more reaction in a shorter period of time. Prior to industrialization, carbonic acid was the major cause of decay of marble and other natural stone used in construction (Gauri and Holdren, 1981). Sulfuric and nitric acid have since replaced carbonic acid as the major cause of decay (Bubenick, 1984).

Yocom, 1979, in his study of air pollution damage to buildings on the Acropolis described four mechanisms by which air pollutants damage natural stone:

- 1) Abrasion-solid particles of sufficient size traveling at high speed may cause destructive abrasion.
- 2) Deposition and removal-solid particles on the surface may not cause any damage other than discoloration, but removal of deposits causes some deterioration. The presence of these particles on the surface can enhance the effects of pollutant gases by providing a large number of reaction centers.
- 3) Direct chemical attack-reactions on the surface of structures results in the dissolution or conversion of calcite to soluble gypsum or calcium nitrate.
- 4) Indirect chemical attack-absorption of chemical pollutants such as SO_2 which may then be converted to sulfuric acid damages the absorbing material.

In addition to the air pollution mechanisms, Yocom noted several other factors that strongly influence the rate of deterioration. Moisture is required to convert SO_x and NO_x into their respective acids. Little decay occurs in the absence of moisture. Temperature also plays an important role. An increase in temp-

erature results in an increase in reaction rates. Furthermore, a surface which is below dewpoint temperature will cause surface condensation enhancing reactions involving soluble pollutant gases. A final factor involves freezing and thawing. Cycles of freezing and thawing cause cracks and spalling on stone resulting in the exposure of new surfaces to chemical attack by reactive pollutants. Combination of one or several of the air pollution mechanisms with these factors is the main cause of accelerated decay.

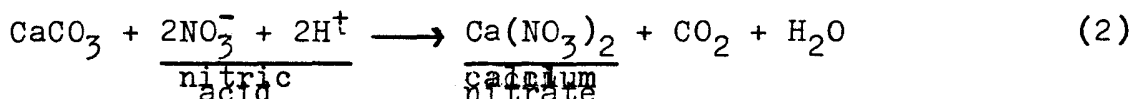
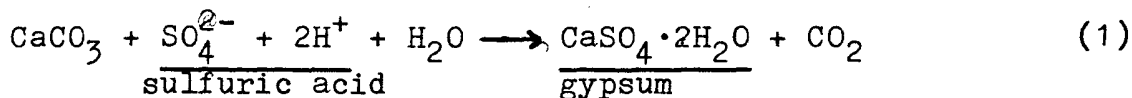
The rate of decay of stone buildings and monuments is also affected by the physical structure of the stone comprising the structure. The rate of all liquid-solid reactions is enhanced by increasing the surface area of the solid exposed to the reaction solution (Bricker, 1984). Therefore, finely crystalline stone is more susceptible to deterioration at the surface because of larger surface area per crystal available for reaction (Bricker, 1984). Porosity of the stone is another important factor. Fine-grained stone with secondary minerals within interstices show less chemical weathering than fine-grained stone with higher porosity (Gauri and Holdren, 1981). Thus, the physical makeup of the stone is an important factor in the rate of decay of stone and must be considered along the previously noted factors in determining the effects of acidic pollutants on stone.

Studies of Structures Affected by Acid Precipitation

Marble and Limestone Structures

Structures composed of marble and limestone affected by acid precipitation have been studied extensively. Marble and limestone are composed primarily of the mineral calcite, which reacts with sulfuric and nitric acids to form more soluble compounds of gypsum

and calcium nitrate(Gauri and Holdren, 1981; Winkler, 1982; Cheng and Castillo, 1984). The respective reactions may be represented by the following equations(Gauri and Holdren, 1981; Cheng and Castillo, 1984):



Thus, equations (1) and (2) represent the reactions of marble and limestone with acid rain forming soluble products which may be washed away more easily upon direct exposure to rain(Gauri and Holdren, 1981; Winkler, 1982). In arid climates or during dry spells, acidic pollutants accumulate as particulate matter on stone surfaces(Gauri and Holdren, 1981) or may be absorbed into the stone(Yocom, 1979) to be activated later by contact with moisture.

Two major forms of damage to marble and limestone have been observed: the type that results from direct exposure to precipitation and the type that results when the stone is protected from direct precipitation.

The weathering and deterioration of stone directly exposed to precipitation is less than that experienced by sheltered stone (Gauri and Holdren, 1981; Winkler, 1982; Yocom, 1979). The precipitation of acid rain results in an acidic solution around calcite grains(Gauri and Holdren, 1981). Dissolution along grain boundaries enlarges intergranular spaces allowing more penetration of the acidic solution and may eventually lead to the sanding of

individual grains leaving behind a surface with a sandpaper-like texture(Winkler, 1982; Cheng and Castillo, 1984). Any gypsum that is formed during the reaction with acid rain is quickly washed away from these surfaces(Yocom, 1979; Gauri and Holdren, 1981). The end result is a slow deterioration of surface detail. In some cases, layers of reprecipitated calcite 2-4 mm thick exist on the surface(DelMonte et al, 1981; Cheng and Castillo, 1984). The overall result of this type of weathering is a slow rate of decay and the loss of surface detail.

The deterioration of marble is much more pronounced in areas protected from direct precipitation(Yocom, 1979; Gauri and Holdren, 1981). On these surfaces, rain is unable to wash away the soot or the gypsum which may have formed in reactions with acidic moisture. The result is the build-up of crusts of gypsum, calcium nitrate, and soot(DelMonte et al, 1981; Gauri and Holdren, 1981). The soot not only discolors the surface, but is rich in sulfur and may also contain catalysts capable of transforming SO_2 into sulfates. The sulfates form sulfuric acid in contact with moisture which dissolves the calcite(DelMonte et al, 1981; Cheng and Castillo, 1984). The gypsum may also penetrate intergranular spaces by capillary action(Winkler and Singer, 1972; Gauri and Holdren, 1981). Crystallization of the gypsum within the pore spaces may exert pressures great enough to cause the disruption of the stone (Winkler and Singer, 1972). Crusts of gypsum and soot may become exfoliated or fall off in layers with continued weathering thereby obliterating surface detail as well as exposing fresh surfaces to chemical attack(Gauri and Holdren, 1981). Crusts generally range in thickness from 2-5cm in humid climates(Cheng and Castillo, 1984).

In arid climates, similar crusts build up with a greater thickness. For example, sculptures on the Acropolis have a gypsum layer of approximately one centimeter thickness(Gauri, 1978). Gypsum crusts may also react with salts from winter spreading forming efflorescences of sodium sulfate on the surface of the marble. If the marble is porous, the sodium sulfate may go beneath the surface and become hydrated, possibly shattering the stone(Winkler and Singer, 1972; Gauri, 1978). In summary, this type of weathering is responsible for much more damage than the weathering under direct precipitation.

One more feature of marble, the interaction of acidic weathering and locked in stresses may greatly accelerate the dissolution process(Winkler, 1982). Winkler noted in his 1982 study that most locked in stresses are released when the stone is quarried, but some do remain. He also noted that ribbed columns have an accelerated rate of weathering and are associated with deep cracks that parallel the ridges regardless of foliation within the stone. Winkler concluded that the rock was weakened by circumgranular dissolution which caused cracks to open up along the edges and ribs. The cracks relieved the locked in stresses, but also permitted easy entry for rainwater, resulting in more dissolution and deepening of the cracks.

True limestones such as Indiana Limestone show surface roughening when exposed to acid rain. The actual amount of surface reduction of the limestone may be measured between resistant shell fragments(Winkler, 1982). The same processes that affect the calcite of marble also affect the calcite of limestone, but to a somewhat lesser degree.

Calcareous Sandstone

The calcite of calcite-cemented sandstone is also subject to attack by acid rain. Dissolution of the calcite by sulfuric or nitric acid in this case results in sanding and may eventually cause the stone to crumble(Winkler, 1982). Statues at Herten Castle near Recklinghausen, Westphalia, Germany composed of Baumberg Sandstone have nearly been completely destroyed as a result of acidic precipitation(Winkler, 1975). Most sandstone is porous and allows solution migration through the pore spaces. As a result of this porosity, secondary reintroduction of calcite may occur causing differential solidification forming a honeycomb structure(Winkler, 1982). For example, calcite was leached from the mortar and redeposited on the surface of the sandstone on the east face of the Freiburg Cathedral, Freiburg, Germany(Winkler, 1982). Therefore, the deterioration of calcareous sandstone buildings and monuments may occur at faster rates as a result of the sandstone's high porosity.

METHODS OF PRESERVATION AND PROTECTION

One obvious method of preserving stone buildings and monuments from acid precipitation is reducing the emissions of SO_x and NO_x to levels which result in a pH of about 5.6, the lowest acidity possible for precipitation from the atmosphere(Bubenick, 1984). This reduction would mean installation of air purifying filters and strict regulation of industry and transportation, both of which would result in high economic costs(Bubenick, 1984). The regional nature of acid rain also presents a problem. Different countries have different standards for "clean air", the end result

being a problem of international regulation(Likens and Borman, 1974). Thus, alternative solutions must be found.

Local control of emissions may provide a means for lowering SO_x and NO_x levels for areas closest to the sources. Yocom,1979, cited several possible controls on local emissions affecting the buildings on the Acropolis. His proposals included that all new houses be electric or solar heated and that all internal combustion vehicles be prohibited in the area of the Acropolis. Regulation of this type will only have a very localized effect on the concentration of acidic pollutants and can not be considered a solution to the regional problem of acidic deterioration of natural stone buildings and monuments.

The solution must rest in the treatment of the stone itself. Gauri, 1978, outlined several methods of restoring and preserving stone in his study "The Preservation of Stone." The objective of these methods is to increase water repellancy at the surface while enabling water within the stone to move outward.

The first step in the restoration of stone is the cleaning of the stone. There are both mechanical and chemical methods for cleaning stone. Mechanical cleaning involves brushing, blasting with air, water, or grit, or scrubbing to remove soot and gypsum layers until the sulfate ion concentration has been reduced to 0.3% by weight of the stone. Chemical cleaning of the stone should be used as a last resort. Alkaline cleaners leave behind traces that form efflorescences, and all penetrate deep into the stone causing it to weaken and corrode.

Once the stone has been cleaned, three possible methods of consolidation and preserving stone from future chemical attack

consist of 1) replacement of constituents prone to atmospheric attack, 2) precipitation of chemically resistant material within the pore spaces of the stone, and 3) treatment with organic monomers and prepolymers.

The first process involves the replacement of minerals susceptible to atmospheric attack. For example, the introduction of barium hydroxide ($\text{Ba}(\text{OH})_2$) into weathered marble results in the replacement of the calcium of the calcite or the gypsum, forming less soluble barium carbonates and sulfates or a solid solution between the two. The problem with this method is that reaction rates are slow, and the reaction does not penetrate deeply enough into the stone.

A second possible method of protection of building stone is the precipitation of chemically resistant minerals within the pore spaces of the stone. Silicon dioxide, SiO_2 , can be deposited from water soluble organic silicates or from silicon esters. The deposited silica bonds with the silica of the stone when done correctly, and should therefore, should be confined to sandstones and other building stones consistion of silicate minerals. This treatment has one drawback. Rapid precipitation is necessary or else the liquid moves to the surface where precipitation occurs forming a crust harmful to the building stone.

Treatment with organic monomers and prepolymers is probably the most feasible method for restoring and preserving stone. Once these organic substances are introduced into the stone, polymerization occurs as a result of a curing agent injected into the stone. The effects of monomers and prepolymers is to recement dislodged grains and to enhance water repellancy. The polymer

must penetrate the stone to a depth greater than the zone of weathering without completely filling the pore spaces. The stone has to be able to "breathe." If the pores are plugged, then there is water trapped behind the treated zone, which may eventually cause disintegration of the treated stone. There are other possible disadvantages as a result of this treatment. If the polymers absorb active gases, they may actually increase the rate of stone decay. Marbles treated with epoxy resins deteriorated faster than untreated marble in an atmosphere containing SO_2 . Investigation revealed that resins possess pores 1-2 nanometers in diameter whereas SO_2 has a diameter of 0.5 nanometers. Thus, the sulfur was easily absorbed by the marble accelerating its decay. Absorption of ultraviolet radiation causes the polymer to decay, eventually leaving the stone unprotected. A polymer that does not absorb ultraviolet radiation that penetrates the earth's atmosphere to ground level is needed. Studies of fluorocarbons indicate that they may be suitable for this use. Early signs of decay of polymers include the development of a yellow film. Epoxies in the environment show degradation in six months. Fluorocarbons in the same environment have shown no change after five years of exposure.

Thus, the best treatments involve low density polymer impregnation which lines the pore spaces, but does not completely block movements of liquids and gases within the stone. Absorption of water in the best treatments (treatments with fluorocarbons) is reduced by one-half. It should be noted that treatments usually affect one property adversely while improving another.

SUMMARY

Acid rain has become an international problem affecting large geographic regions. Acid rain not only affects the environments but also causes accelerated decay and deterioration of natural stone buildings and monuments in these regions. SO_x and NO_x are the two major pollutants contributing to the acidity of precipitation. Their major sources include fossil fuel combustion for energy and transportation needs as well as other industrial processes such as metal processing. As a result, the pH of precipitation has declined to average values ranging from 3-5. This increased acidity has accelerated the decay of natural stone structures, especially those composed of marble, limestone, or calcareous sandstone. Regulation of emissions from industry and transportation does not seem to be a plausible solution to protect the stone. Rather, treatment of the stone with fluorocarbon polymers appears to be the best method of preservation and protection of the stone. Acid rain will continue to be a problem in the future. Additional research on the protection of stone is needed so that ancient, as well as modern architectural structures, sculptures, and monuments composed of natural stone can be preserved for future generations of people in an environment frequented by acid rain.

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