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REVIEW ARTICLE

The Significance of Air Pollution in the Process of Stone Deterioration

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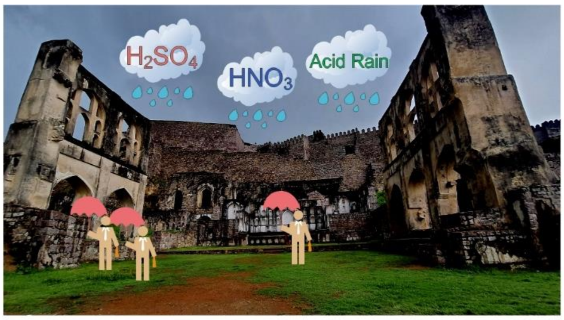
Abstract: Stone materials used in monuments, structures, and sculptures are highly vulnerable to the effects of air pollution. Sulphur and nitrogen oxides are among the most harmful pollutants, especially for carbonate stones. When these oxides come into contact with atmospheric moisture, they form acids that gradually corrode the stone's surface, weakening its structural integrity. These acids may also react with solid particles in the air, such as heavy metals and salts, to create black crusts that blemish the stone's original appearance. These crusts not only compromise the structural stability of the stone but also pose a significant threat to the preservation of important monuments and buildings. Our research shows that stone structures exposed to air pollution for extended periods can provide valuable insight into historical pollution levels through their weathering crusts. These findings offer important insights for improving long-term geochemical records and restoring past air quality conditions. Additionally, this methodology can enhance the study and preservation of stone weathering while enabling more accurate reconstructions of historical pollutant levels.



Keywords: *Stone, surface, air pollution, calcium carbonate, monument.*

Contents

1. Introduction

Materials science encompasses a wide range of substances and their applications.[1-3] Throughout history, epochs have been named to reflect human progress intertwined with the evolution and utilization of materials.[4-6] While materials may lack inherent functionality in isolation, their absence renders human endeavors futile.[7-9] Nature has harnessed atomic hierarchies similar to those employed in human-made structures over time.[10-12]

In contemporary society, sustainable development is a pivotal concept.[13-15] Its significance lies in its potential to ensure equitable utilization of resources and foster harmonious interaction between humanity and the ecosystem.[16-18] Therefore, the discovery and innovation of exceptional materials are paramount in our era of progress.[19-21] These materials find application across various branches and subfields of analytical chemistry, facilitating identifying and analyzing substances with complex patterns. The quality of material required for such analyses, known as the "minimum volume," plays a critical role.[22-24]

Abhishek Singh is an accomplished professional in the field of mechanical engineering with a focus on air quality management. With a background in engineering, he has dedicated their career to developing innovative solutions for air emission control. Their expertise spans the fabrication of air emission control units, including designing and implementing systems to reduce pollutants and mitigate environmental impact.

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The system provides convenience, simplicity, and outstanding life-sustaining components, meeting universally accepted standards.[25-27]Numerous industrialized nations' economic advancement and sustained growth owe much to such materials.[28-30] An analysis delves into utilizing natural resources and active substances.[31-33] This involves employing various approaches, tools, and strategies as integral developmental components.[34-36] This juncture is pivotal in advancing current scientific understanding and holds promise for future applications across various fields.[37-39]

Throughout history, the material of preference has often been a defining factor in various periods.[40-42] From the Stone Age to the Steel Age, epochs have been demarcated by significant material shifts, albeit somewhat arbitrarily.

As an enduring and environmentally friendly natural substance, stone is cherished in human culture.[43-45] Its usage as a construction material dates back to antiquity, manifesting in structures such as stone walls, barrows, and rune stones during the Stone Age. Even today, the construction industry continues to rely on this versatile material.

Environmental pollution is the depletion of energy or matter from the earth's renewable resources, such as air, water, or land.[46] This depletion harms the environment and its ecological well-being, affecting people's lives in terms of quantity and quality.[47] Activities like mining, farming, and manufacturing can contribute to this damage. Urbanization adds to the environmental challenges, making smart cities a potential solution.[48] Improving the accuracy of air quality data is essential for epidemiological investigations, as air pollution levels can vary significantly across different regions and over time.

There has been an alarming increase in the release of air pollutants into the atmosphere, including persistent organic pollutants (POPs).[49] POPs are harmful because they resist various biochemical and photolytic breakdown processes persisting in the atmosphere, soils, and sediments. Due to their high toxicity and long-lasting nature, POPs accumulate in the adipose tissues of humans and wildlife, resulting in observable changes related to growth, development, and reproduction.[50] POPs pose a significant threat because of their poisonous, bioaccumulative, and persistent nature and their ability to travel long distances from various sources.[51]

The degradation of stone materials is closely linked to air pollution, with urban areas experiencing high levels of human-caused emissions exacerbating this issue.[52] Studying the effects of atmospheric pollution on outdoor cultural heritage is of significant interest. Additionally, preserving world heritage is a crucial focus of various UNESCO initiatives.[53]

Extensive research efforts have been focused on the deterioration of stone materials for decades, especially concerning preserving cultural heritage.[54] It is essential to understand the mechanisms behind this phenomenon to develop effective and long-lasting conservation strategies. Air pollution, particularly in urban areas, where sulphation processes are predominant, is a significant factor in stone decay.[55]

It is generally agreed that the primary mechanisms of deterioration related to pollution involve the formation of gypsum ($CaSO_4{\cdot}2H_2O$) and carbonate dissolution.[56] However, there is still much debate surrounding the weathering of limestone crusts, which occurs when calcium carbonate ($CaCO_3$) transforms into calcium sulfate ($CaSO_4$) due to air pollutants and anthropogenic sulfur deposition.[56] This accumulation of calcite and gypsum crystals on the stone's surface gradually erodes it. Despite efforts to reduce SO_2 concentrations in recent decades, weathering crust degradation remains a persistent issue. These crusts periodically fracture, revealing the extent of the damage and exposing a pristine surface underneath. The corrosion of stone materials caused by acid rain as shown in Figure1, resulting from pollution of rainwater with carbon oxides (COx), nitrogen (N), sulfur (S), and leads to the deterioration of rock-making minerals.[57] Pollution has become a complex issue, with rising levels of particulate matter intensifying the acidic effects through dust deposition.[58]

Figure 1. *Adverse impact of acid rain*

Weathering crusts are made up of afresh designed minerals such as gypsum. These minerals incorporate atmospheric particles, including sleek aluminosilicate particles, porous carbonaceous particles (soot), and metal particles primarily composed of iron.[59]The sources of these atmospheric particles are diverse and may include combustion of fuel from power plants and residential heating, combustion of coal, and the emissions from petrol oil.[60] Additionally, sources such as vehicle exhaust[61] and biomass combustion[62] have been identified.

Stone decay can occur due to a combination of chemical, physical, and biological factors that frequently work together. Water acts a crucial role in both weathering and co-agent functions. It acts as a solvent by dissolving specific components such as gypsum, which are soluble in water. Water can cause stone degradation by carrying salts or pollutants onto the surface or penetrating its porous structure. Additionally, water creates favorable conditions for microbial nutrients, mainly when interacting with composites from the substrate of stone (e.g., carbonates) or atmospheric NOx contaminants, thereby facilitating biological decay. In general, degradation methods are predisposed by various factors such as environmental conditions, materials, strategy, construction methods, and preservation practices. Among these, environmental factors notably play a significant role in the decay procedures of stone.[63] Aspects like building orientation and architectural intricacies also play a role in determining how moisture source and drying affect deprivation.[64]

Acknowledging that environmental factors can lead to changes in all types of stone materials is crucial. However, human activities, such as the emission of pollutants, can speed up this process. This review will concentrate on the importance of air pollution on in the degradation of stone, especially the darkening of buildings in heavily polluted urban areas.

2. Historical Episode

The Cologne Cathedral is an important cultural monument in northern Europe, but it is facing significant stone degradation. Different types of building stones within the cathedral are experiencing various weathering circumstance. The Drachenfels trachyte, utilized in the medieval construction phase, exhibits evident structural deterioration and an extensive formation of gypsum crusts. Various researchers have explored the environmental and geological factors contributing to the degradation of the building stones in Cologne Cathedral.[65,66] In the 1970s, a research program was conducted to investigate the effects of air pollutants, specifically, the impact of flue gas on the deprivation of ordinary building stones and possible methods for protective conservation will be explored.[67] Further studies focused on various deterioration processes affecting natural building stones within Cologne Cathedral.[67,68] Some researchers found negative interactions between different types of stones used in the construction, which were primarily deteriorating the sandstone and consequently affecting the neo-Gothic architectural construction.[69,70]

The building stones have suffered significant deterioration, which is particularly noticeable in the situation of the Drachenfels trachyte.[71] The stones are covered with black framboidal crusts, laminar, and thin, laminar that contain particles from contamination deposits. Additionally, weathering crusts have formed on silicate stones, which subscribe to the mortification of the historical building substantial. It is noteworthy that crust creation on the Drachenfels trachyte powerfully associates with stone disintegration. Gypsum is found not only in the crusts but also in extensive layers of deteriorating stone material. These crusts have a tendency to detach, exacerbating the structural deterioration.

The Drachenfels trachyte exhibits characteristic decay features like contour scaling, flaking, and exfoliation, resulting in gritty decomposition and deteriorate. Weathering crusts develop on Stenzelberg late and Obernkirchener sandstone in narrow layers, usually around 2–3 mm thick, which are susceptible to get detachment from the surface of stone. Schlaitdorfer sandstone displays dense black crusts, frequently lead by extensive contour rise measuring some centimeters wide and notable granular erosion. For Krensheimer Muschelkalk, these crusts provide temporary stabilization to the stone surface.[72] Exposed surfaces subjected to rain may display solution phenomena like microkarst formations. Surfaces exposed to rain may exhibit solution situation such as microkarst.[71]

Thin slices of crust samples were collected from buildings in various cities across Northern Italy. These samples were then examined using both optical and electron microscopy techniques. The investigation revealed some key findings[73] that can be summarized as follows:

- Elevated concentrations of black carbonaceous particles from fuel oil consistently appeared within the calcite gypsum mixture.
- Coal-derived carbonaceous particles were not commonly detected in the samples.
- There is a direct correlation between the thickness of the crust and the quantity of black particles from oil-fired sources found within it.
- Black particles are predominantly associated with gypsum and are frequently observed to be embedded within it.
- On occasion, the orientation of gypsum crystals suggests growth around the surfaces of the black particles.

The theory suggests that soot particles from oil combustion have a significant impact on stone sulphation in urban environments. This aligns with several experimental findings conducted at the Lawrence Laboratory in Berkeley. The experiments showed that carbonaceous particles catalyze the oxidation of SO_2 to sulfate when present in liquid water.[74] Furthermore, it has been observed that the catalytic oxidation of SO_2 on carbonaceous particles suspended in water remains largely unaffected by the pH levels encountered in urban atmospheres.[75] Under laboratory-simulated environmental conditions, a direct correlation has been established between the reaction rate and the concentration of suspended carbonaceous particles. However, no significant correlation was found with the concentration of dissolved SO_2.[75] This implies that under similar conditions, the rate of sulphation is approximately proportional to the concentration of black carbonaceous particles deposited on wet stone, yet shows little dependence on airborne SO_2 levels. It is important to note that trace metal catalysis may influence the sulphation rate. However, crust samples from Venice, where damage is most pronounced, contain these metals at much lower concentrations than samples from other cities.[73] The absence of motor vehicle traffic in Venice explains this discrepancy.

Air pollution has been a major concern since the beginning of the Industrial Revolution. It has significantly affected human well-being, habitat, and the integrity of stone. The root cause of this problem is human activity, especially the burning of wood and fossil fuels, which liberate various solid and gaseous chemicals within the atmosphere. The main culprits behind the certain oxides in stone materials' degradation undergo reactions with water, resulting in acidic conditions. These oxides include carbon dioxide (CO_2), sulfur oxides (SOx), and nitrogen oxides (NOx).[76] These acids interact with stone surfaces, particularly carbonate-based materials like marble and limestone, causing them to deteriorate. CO_2 reacts with water through the following reactions:

$$CO_2 + H_2O \longleftrightarrow CO_2 \,.\, H_2O \quad (1)$$

$$CO_2 \,.\, H_2O \longleftrightarrow H^+ + HCO_3^- \quad (2)$$

An increase in atmospheric CO_2 leads to higher levels of CO_2 in water, which increases its acidity. $CaCO_3$, which is commonly found in stone materials, has low solubility in water, but this solubility increases with dissolved CO_2.

$$CaCO_3 + CO_2 \,.\, H_2O \longleftrightarrow Ca(HCO_3)_2 \quad (3)$$

Henry's law explains that the levels of CO_2 in the environment and the temperature of the water play a significant role in the solubility of CO_2 in water. Lower temperatures increase the rate of dissolution, leading to an increase in carbonate dissolution in urban areas with high CO_2 levels and during the winter season when temperatures are lower. Equation (3) shows that the state of equilibrium can be changed towards the reactants by water evaporation or a temperature rise resulting in the regeneration of calcium carbonate. $CaCO_3$ can dissolve and precipitate in the same location or other areas, leading to significant changes in the microstructure of the stone in the dispersed regions, making it more prone to further degradation.

The atmospheric CO_2 level is expected to rise to about 700 ppm in 100 years based on the Keeling curve, compared to the current level of around 420 ppm.[77] This increase has a relatively small impact compared to the 2500 ppm level of CO_2 found in indoor settings. Dissolving CO_2 can pose a threat to fragile and expensive surfaces of wall paintings that contain calcium carbonate in the setting layers or pigments.[78]

$$O_2 \longleftrightarrow 2O \quad (4)$$

$$N_2 + O \longleftrightarrow NO + N \quad (5)$$

$$O_2 + N \longleftrightarrow NO + O \quad (6)$$

$$OH + N \longleftrightarrow NO + H \quad (7)$$

At temperatures above 2200 K (~1900 °C), the initial reaction (Equation (4)) occurs, followed by responses (Equations (5)-(7)). Therefore, nitric oxide (NO) generation requires high temperatures and an excess of oxygen in a particular area, such as in interior combustion machine. Additionally, NO can undergo conversion to NO_2 via a reaction with ozone.

$$NO + O_3 \longleftrightarrow NO_2 + O_2 \quad (8)$$

NO_2 can react with oxygen to produce dinitrogen pentoxide (N_2O_5), which can then dissolve in water (H_2O) to form nitric acid (HNO_3).

$$N_2O_5 + H_2O \longleftrightarrow 2HNO_3 \quad (9)$$

The acid described can undergo a chemical reaction with $CaCO_3$.

$$2HNO_3 + CaCO_3 \longleftrightarrow Ca(NO_3)_2 + H_2O + CO_2 \quad (10)$$

HNO_3 can corrode the stone substrate, which can result in the creation of $Ca(NO_3)_2$. This substance has a greater solubility in comparison to carbonates. This reaction cannot be reversed, Unlike Equation (3), and the process does not involve any carbonate re-precipitation at the end.

SO_2 is a major threat to the preservation of stone materials. It is predominantly produced by human pursuits, particularly the burning of fossil fuels like dense parts of mineral oil and coal. When SO_2 undergoes oxidation from S(IV) to S(VI), it can take various pathways involving NO_2, O_3, metals, and particulate matter (PM_1, $_{2.5}$, and $_{10}$).[79] This chemical process leads to the formation of sulfur trioxide (SO_3), which subsequently interacts with H_2O to generate sulfuric acid (H_2SO_4). As a result, H_2SO_4 interacts with $CaCO_3$, leading in the formation of CaSO4.

$$H_2SO_4 + CaCO_3 \longleftrightarrow CaSO_4 + CO_2 + H_2O \qquad (11)$$

$CaSO_4$, which is often found in the hydrated arrangement of $CaSO_4 \cdot 2H_2O$, has a solubility that is similar to calcium carbonate. When $CaSO_4$ precipitates, it forms a crust. While NO_x and SO_2 emissions have decreased in recent years, they still remain high in countries like China and other emerging nations.[80] Therefore, the technique described in Equation (11) remains crucial in such settings.

Particulate matter (PM) is a type of air pollution that consists of small particles and liquid droplets. These particles can include acids, metals, dust, soil particles, and organic compounds. PM comes from both natural sources such as volcanoes, sea spray, and dust storms, and artificial sources such as industrial and mechanical operations and automobile emissions.[81]

The contaminants listed in Equation (3), (10), and (11) can be deposited onto a stone's surface through either wet or dry processes. Dry deposition happens when gases and particle matter settle on a surface without water. In contrast, wet deposition occurs when atmospheric gases and particulate matter combine with water and are removed through precipitation, such as fog or rain. It appears at a slower pace but maintains a greater level of consistency, while wet deposition is quicker and more effective. Water functions both as a solvent and occasionally as a reactant during the process and facilitates the reactions involving the substrate mentioned in Equations (3), (10), and (11).[82]

$CaSO_4$ can be effectively eliminated from stone surfaces through washing since it exhibits higher solubility than $CaCO_3$. Nevertheless, these deposits tend to accumulate and amalgamate with particulate matter, frequently developing dark crusts in sheltered areas. The colour of deterioration byproducts can range from grey to white and is influenced by the concentration of PM present. The ICOMOS Glossary defines a "black crust" as a generally cohesive collection of elements on the surface. It may consist of exogenic deposits and elements originating after the stone. These crusts usually appear dark in colour but can also exhibit bright hues. Crusts can either have a consistent thickness, mimicking the stone surface, or an uneven thickness that may obscure the features of the stone surface.[83]

3. Cultural Heritage

Cultural heritage plays a crucial role in human civilization, reflecting important social development processes. It is tangible evidence that is necessary for the sustainable progress of society. Protecting our cultural heritage is fundamental to nurturing social and artistic advancement.

Atmospheric pollutants pose a significant risk to heritage materials, particularly stone, resulting in substantial losses beyond economic implications. The impact of air pollution on immovable heritage as shown in **Figure 2.**

Air pollution, which includes gaseous and fine particulate matter pollutants, is a major threat to the sustainable preservation of cultural heritage. Acidic and oxidizing gases in air pollutants cause severe corrosive effects on heritage materials such as stone, wood, metals, and paints, through acidification and oxidation reactions.

Acidic and oxidizing substances present significant dangers to the preservation of ancient buildings and monuments. Acidic substances such as acid rain and industrial emissions chemically react with stone materials like limestone and marble, causing erosion, pitting, and decreased structural strength. They gradually degrade the surface and erode intricate features by reacting with the calcium carbonate in the stone. Similarly, oxidizing chemicals like ozone and chlorine hasten the decomposition of organic substances and contribute to the erosion of metals, compromising the strength of structural components and decorative features. Furthermore, these treatments induce surface deterioration, altering the original aesthetic of the monuments. To counter these detrimental effects and ensure the cultural and historical importance of these monuments for future generations, it is imperative to implement effective conservation techniques, such as monitoring, protective coatings, and new treatments.

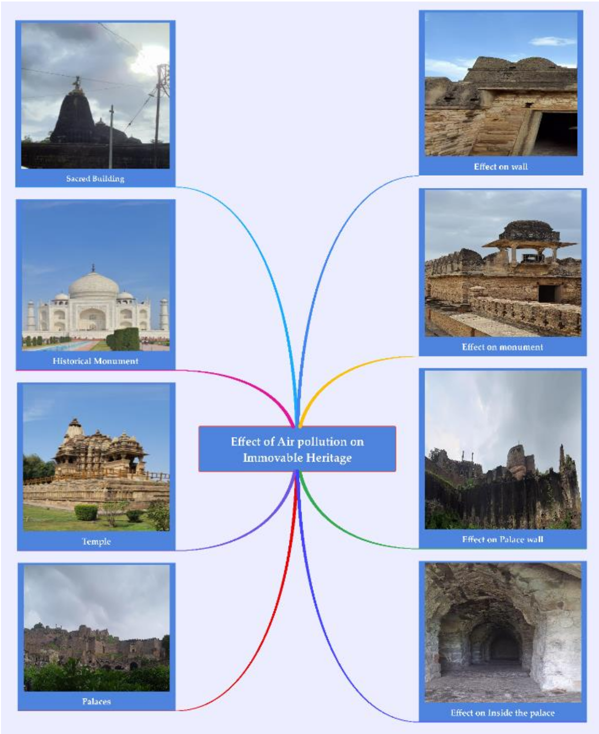

Figure 2. *Effect of air pollution on immovable heritage*

4. Damage to monuments

Did you know that monuments can suffer from various types of deterioration? To help understand this better, we have categorized these types into eight groups, which are shown in Figure 3. By being aware of the different types of deterioration, we can take proactive measures to preserve and protect these important cultural and historical landmarks for future generations.

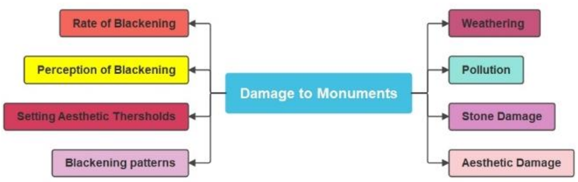

Figure 3. *Different forms of damage to monuments*

4.1. Weathering

Stone structures are subject to a gradual decline over time, commonly known as 'weathering'. Initially, the term 'weathering' referred to the positive effects of weather and drying, but it is now associated with climate-induced damage. Architects and geologists have long recognized how weathering can erode and break down structures. Three hundred years ago, architects believed buildings deteriorated due to 'time, smoke, and weather'.[84]

In areas with mild climate, the most noticeable sign of climate degradation is often frosting damage. When moisture in stone freezes, it leads to a change in volume and causes the outer layers to shatter. Additionally, the presence of salts in the stone and alternating wetting and drying cycles can contribute to similar types of damage. Salts are usually found near the ground but can also be deposited on structures by salty rains, a phenomenon more prevalent in coastal areas experiencing strong winds. Speaking of strong winds, they can directly damage buildings by dislodging tiles and demolishing vulnerable sections of a structure. Although lightning strikes are infrequent, they can cause damage, especially to projecting sections of buildings like steeples.[85] Repetitive exposures to sunlight and subsequent cooling can also create temperature differences that result in the deterioration of stone surfaces. Marbles and granites are more vulnerable to heat compared to porous stones. Calcite in marbles exhibits anisotropic expansion, expanding across one crystallographic axis and contracting along the other two, whereas the primary minerals in granite have varying thermal expansion coefficients.[86]

Preserving historical monuments and buildings is crucial, and the air pollution-induced degradation of stone structures is a complex challenge that demands our attention. Airborne pollutants, such as SO_2 and NO_2, chemically react with atmospheric moisture to form acids like SO_2 and NO_2. These corrosive acids gradually erode the minerals in stone, particularly calcium carbonate in limestone and marble, leading to the deterioration of these precious structures. It is imperative that we address this issue to safeguard our cultural heritage for future generations.

4.2. Pollution

Complaints about buildings getting dirty have been documented since the time of the Romans. However, in the 17th century, the widespread practice of coal in London led to a significantly more serious issue. Architects like Wren and Hawksmoor were troubled by the thick black layers of sulfate that accumulated on structures exhibited to coal smoke.

It is challenging to accurately measure the degradation of building materials over centuries. However, some people believe that the pace of deterioration increased significantly during the 20th century. But before coming to a conclusion, it is crucial to consider that once a building's capabilities are removed, the impact is permanent and cumulative over time. This can make it hard to comprehend the extent of the damage, as we tend to see the effects gradually. It would be more helpful to know the rate of defilement at a specific point in time. While long-term monitoring may be challenging, associating the pace of degradation of monuments in rural and urban regions can demonstrate the significant impact of urban air pollution on building materials.[87]

The relationship between air pollution and its harmful effects on the environment can be quite complex. While cities have seen a decline in corrosive primary pollutants like SO_2 and smoking since the early 20th century, this does not align with the fast and escalating deterioration of structures and monuments that are considered characteristic of this century. It seems that advances in the deterioration rate of the environment have only sometimes accompanied enhancements in urban air quality. There could be several explanations for this. While the overall number of corrosive pollutants in the city air may have dropped, some elements like ozone, nitrogen oxides, and components that make up photochemical smog could not be reduced. These pollutants may accelerate the deterioration of building materials or serve as catalysts to exacerbate the impact of conventional pollutants.[88] Additionally, building materials have a kind of 'memory', and the current degradation results from contaminants that were deposited in the past.[87]

In recent times, the high levels of sulphate deposition have decreased considerably. As of now, the deposits mainly comprise of diesel soot and nitrogen compounds. In the future, the crusts on buildings may show more organic chemistry, which can lead to a change in the color of building surfaces due to the oxidation of the deposited organic material. If we can reduce soot levels in metropolitan areas, it may result in natural cleaning of ancient structures by rain and wind.[89]

4.3. Stone Damage

Numerous studies have investigated the effects of atmospheric contamination, specifically SO_2, on stone as it is widely used in historic buildings. The primary consequences of airborne pollutants on the stone are chemical breakdown, which causes damage to the substance, soiling, blackening, leading to visual nuisance.[90]

Recently, the primary process of deterioration in metropolitan areas was the dry accumulation of SO_2. This was primarily emitted from the ignition of fossil fuels, followed by its conversion into sulphate due to oxidation. Two critical prerequisites are essential for the occurrence of the oxidation process. Firstly, moisture is required on the surface or within the pores close to it. Secondly, an oxidation process is necessary to transform SO_2 into H_2SO_4 or an in-between sulphite (SO_2^-) salt into a sulfate, namely $CaSO_4$ dihydrate. In urban atmospheres, NO_x and other gases can also stick to stone surfaces through deposition. When there is moisture, NO_x can increase the oxidation of SO_2.[88]

A stone's permeability and specific surface area can significantly affect the movement of moisture and the accumulation of pollutants on its surface. The accumulation of air particles can also be influenced by surface roughness. If the pollution results in soluble salts, they can penetrate the stone and cause degradation. Salts present on building surfaces can increase humidity levels within the stone, which can lead to the accumulation of more contaminants.

Stones that contain carbonate are highly vulnerable to the negative effects of contamination. When subjected to elevated concentration of SO_2 contamination, carbonate stones that have not been sufficiently washed by rain can produce a tough outer layer of gypsum, which becomes darkened due to the inclusion of soot particles.[91] The expansion of gypsum within the stone can cause stresses that result in physical damage to the structure in various ways, as gypsum possesses a larger molar volume compared to $CaCO_3$. Carbonate stones that are frequently and intensely exposed to rainfall can also undergo a dissolving process on their surfaces. The breakdown occurs more rapidly when the stone has been previously exposed to air contaminated with sulfur dioxide (SO_2).[91]

Dolomite-containing carbonate stones ($CaMg(CO_3)_2$) undergo a reaction with SO_2 to yield $CaSO_4$ and $MgSO_4$. As a result of this reaction, $CaSO_4$ forms a coating of soot and gypsum, while magnesium sulphate, which is highly soluble, can cause more extensive damage due to the crystallization process of this particular salt penetrating deeper. Calcareous sandstones are prone to erosion in heavily polluted areas due to the corrosive effects of atmospheric sulfuric acids. The dissolution of calcite in small quantities can release numerous sand grains, aggravating the damage caused by the crystallization of this particular kind of salt.[86]

Sandstones composed primarily of quartz exhibit high resistance to sulfuric acids but are prone to accumulating significant dirt.[86]

Acidic gases can have a significant impact on certain categories of roofing slates. If the slate comprises calcite, when SO_2 dissolves in rainwater, it reacts to generate an acidic solution, which can be retained by capillary action within the crevices of the slate and corrode the calcite. This interaction can also cause the formation of gypsum crystals, which can add to the harm. In situations where the slate includes unstable pyrite (iron sulphide) and calcite, rainwater may combine with the pyrite to produce sulfuric acid. This acidic solution can corrode the calcite and potentially cause the slate to collapse.[86]

Granite is a popular material for building sites because of its durability and resistance to acidic pollutants. However, recent research suggests that it can still be damaged by air pollution.[92] There are two types of damage that granite surfaces can experience: gypsum crusts from airborne contaminants and weathering layers of clay-calcitic elements inherent to the granite's composition. In regions with high humidity and temperate climates, air pollution containing SO_2 can have a twofold effect on the deterioration of granite.[93] It can cause sulphate precipitation and convert feldspars into kaolin. Moreover, the process of plagioclase weathering can provide the necessary Ca^{2+} ions for forming gypsum crystals.

4.4. Aesthetic Damage: Blackening

In the past few decades, there has been a significant reduction in the levels of acidic pollutants, resulting in fewer chemical reactions and surface degradation of stones. However, this has resulted in an increase in the prominence of the problem of darkening or soiling of building materials, which has led to greater attention being paid to aesthetic factors.

Buildings can darken due to the accumulation of particle debris caused by fine carbonaceous particles that cover their exposed surfaces.[94] This is an aesthetic problem that has been a concern for centuries, dating back to ancient times. For instance, the defacement of sacred structures in Ancient Rome was a significant concern for the poet Horace. In the 17th century, John Evelyn also expressed significant concerns about the unsightliness caused by the accumulation of soot on buildings in London.[84] The carbonaceous deposits on building surfaces have high optical absorptivity, making them highly efficient in darkening surfaces.[95]

It is noteworthy that even in the latter part of the 20th century, blackening remained a problem.[96] While coal usage decreased in many cities, diesel soot became the primary contributor of elemental carbon. Even to this day, there is ongoing concern about this issue. However, some regions have experienced a decline in soot in the air, resulting in cleaner surfaces. Rain also plays a significant role in washing away pollutants, which has led to cleaner buildings in some cases.[89] Nevertheless, biological activity can significantly worsen the blackening of stone surfaces, especially when combined with increased organic pollution.[97]

4.5. Rate of Blackening

The rate at which monuments become darkened by air pollution is determined by several critical factors. Urban areas with heavy industrial activity and high traffic often experience accelerated darkening due to elevated levels of pollutants such as soot and sulfur dioxide. The choice of materials for monuments is also crucial; porous stones like limestone and marble are more susceptible to damage than sturdy materials like granite. Environmental elements, such as humidity, temperature fluctuations, and precipitation patterns, also impact the rate at which pollutants settle and react on the surfaces of monuments. Implementing efficient maintenance practices, such as applying protective coatings and regular cleaning, can slow down the darkening process. To maintain the visual and structural integrity of monuments in the face of ongoing environmental challenges, it is essential to implement proactive conservation measures and enforce strict air quality laws.

According to a study, when analyzing lengthy data records to understand the blackening process, the bounded exponential fit model is a more precise model than others.[98] Rather than using a reflectance meter to detect color variations, a colorimeter is often used as it provides more comprehensive information.

Materials can turn yellow due to various processes like sulphation,[90] deposition or oxidation of organic compounds, or iron.[99] If the atmosphere remains contaminated with organic pollutants, the yellowing process may become more pronounced, especially for materials that are prone to damage.

4.6. Perception of Blackening

The human eye can distinguish between clean and dirty areas on a white surface when 0.2% of the surface is covered by dark particulate matter.[100,101] In a study by Lanting,[95] it was found that complaints are likely to arise when the coverage reaches 2%, and they become more severe at 5%. A more recent study by Bellan *et al.*[102] discovered that observers can only identify that a sample is getting dirty when black carbon particles cover the surface to a level of 2.4%. However, when it comes to buildings, the problems become more complex, especially within a specific setting.

Several individuals had concerns about the cleanliness of the buildings. They formed their opinion based on specific old structures that displayed stark contrasts between clean and dark (sometimes green) areas. At times, entire facades were covered in thick soot. Visitors were more inclined to notice changes in brightness rather than color or saturation, which do not vary significantly with respect to the stone used.

4.7. Setting Aesthetic Thresholds

It is crucial to understand what level of blackening is acceptable for managing air pollution and maintaining the aesthetic appeal of structures. To determine the permissible concentrations of elemental carbon (EC) in the atmosphere, it is possible to calculate the derivative of the sigmoid curve related to perceived lightness, which helps analyze the various segments of the curve and possible thresholds. However, the acceptable levels chosen should take into account the specific political and cultural considerations of the area.

This argument suggests that the color of buildings changes gradually over time, often following an exponential pattern. The study mainly focuses on light-colored stone, which is considered more vulnerable to aesthetic changes. Pollution exposure tends to stabilize the color of buildings at a relatively consistent level after several years. It is hypothesized that dark-colored stones may be more tolerant of higher levels of soot accumulation.

4.8. Blackening Patterns

Blackening patterns are a type of discoloration that do not necessarily cover the entire exterior of a building uniformly. These patterns have been widely considered offensive for a significant period of time. However, there is a need for more studies regarding public perception of blackening patterns. Grossi and Brimblecombe[98] conducted a study to determine the level of acceptance of different blackening patterns, utilizing two desktop efforts that employed a strategy identical to studies in art psychology.

When making decisions, it is important to take into account the effect of perceived lightness versus opinions about unsightly patterns. Although it may be challenging to determine, unattractive patterns can have a significant impact on visitors' experience. To preserve the visual authenticity of historic buildings, it is essential to closely monitor patterns of dirt buildup. This is particularly critical when utilizing selective cleaning methods for stone surfaces.

The impact of air pollutants can obscure the beauty and historical significance of old buildings. This darkening diminishes the cultural and aesthetic value. Conservation efforts are essential to apply cleaning techniques and protective measures, ensuring the preservation of these monuments' authentic appearance.

5. Discussion and Way forward

The occurrence of blackening is a significant issue for stone materials in heavily polluted urban areas. Scientists from various fields such as chemistry, physics, geology, and conservation have extensively studied this phenomenon. Their research ranges from examining the macroscopic to microscopic levels, investigating the structure and composition of affected objects, their interactions with pollutants, and the influence of environmental factors. This report emphasizes the importance of a multidisciplinary approach in understanding the complexity of this subject.

The data collected have significant scientific value and practical applications. Various analytical methods have been used to determine the composition of these blackened crusts. The findings are also valuable for stone conservators, helping them develop effective strategies to protect original substrates and prevent further pollution accumulation. The paper discusses a range of cleaning and conservation techniques, from traditional methods to advanced approaches such as laser cleaning.

Moreover, the research sheds light on the formation process of these crusts, which has social significance. Stakeholders involved in heritage management are encouraged to advocate policies that promote the preservation of cultural assets while addressing environmental concerns such as reducing greenhouse gas emissions.

The research findings also highlight the link between blackening and airborne pollution, positioning these phenomena as indicators of past pollution levels. However, definitive methods for acquiring precise information still need to be discovered. Unresolved questions persist, such as the oxidation of sulfur dioxide and its catalytic processes on stone surfaces, potentially involving additional pollutants like O_3, NOx, metals, or soot. While bacterial involvement has been suggested, the mechanisms remain poorly understood.

There is a critical inquiry into the future implications of predicted pollution patterns on blackening occurrence and broader stone preservation. Decreased emissions of sulfur oxides (SOx), nitrogen oxides (NOx), and particulate matter may reduce blackening concerns over time. However, anticipated climate changes, including rising temperatures, elevated atmospheric carbon dioxide levels, and increased frequency of extreme weather events, introduce uncertainties regarding the preservation of cultural assets. It is conceivable that a new equilibrium will emerge between materials and the environment, shifting the focus from "air pollution - conservation of built heritage" to "climate change - conservation of built heritage."

5. Conclusion

Research into the degradation of stone materials, particularly in urban settings, is crucial for preserving cultural heritage.[103] Air pollution, which is especially prevalent in cities, significantly contributes to stone deterioration.[104] The primary mechanisms driving this degradation are gypsum formation and carbonate dissolution.[105] Weathering crust degradation is also a major issue, which occasionally results in the fracturing of crusts, revealing the extent of damage. Acid rain, which results from the contamination of rainwater by sulphur, nitrogen, and carbon oxides, accelerates the breakdown of rock-forming minerals.

Weathering crusts predominantly comprise newly formed minerals, such as gypsum, that encapsulate airborne particles. These particles encompass three main types: predominantly iron-based metal particles, smooth aluminosilicate particles, and porous carbonaceous particles (soot). Environmental factors, including moisture supply, drying, architectural design, construction practices, and maintenance, significantly influence degradation processes.

The Cologne Cathedral, a prominent cultural icon in northern Europe, is currently facing substantial stone degradation. Specifically, the Drachenfels trachyte exhibits visible structural deterioration and the proliferation of extensive gypsum crusts. Signs of deterioration include contour scaling, flaking, and exfoliation, leading to the dissolution and collapse of its granular structure, with rain-exposed surfaces displaying solution phenomena like microcars formation.

Analysis of crust samples from structures in Northern Italy revealed high concentrations of black carbonaceous particles from fuel oil within calcite and gypsum mixtures. These particles, primarily associated with gypsum, are often enclosed within it. It is theorized that soot particles from oil combustion significantly influence the stone sulphation process in urban environments.

Experiments conducted at the Lawrence Laboratory in Berkeley demonstrated that carbonaceous particles act as catalysts for oxidizing sulphur dioxide (SO_2) to sulphate in the presence of liquid water. A direct correlation between the rate of reaction and the suspended carbonaceous particle quantity was observed under laboratory conditions, with no significant relationship identified with dissolved SO_2 concentrations. Trace metal catalysis may affect sulphation rates, although crust samples collected from Venice showed significantly lower metal quantities than from other cities.

Since the onset of the Industrial Revolution, the issue of air pollution has become increasingly prominent, posing significant threats to human well-being, ecosystems, and the integrity of various stone materials. Certain oxides undergoing chemical reactions with water are primary contributors to stone degradation, resulting in acidic conditions affecting stone surfaces, particularly carbonate-based materials like marble and limestone.

Particulate matter (PM), comprising liquid droplets and tiny particles containing soil particles, metals, acids, dust and organic substances, poses another threat. Originating from both natural and artificial sources, including industrial operations and vehicular emissions, PM can be deposited on stone surfaces via dry or wet processes.

Cultural heritage is paramount in human civilization, yet it faces severe risks from air pollution, leading to substantial losses beyond economic implications. Monument damage can be classified into various categories, including weathering and pollution, with urban air pollution notably impacting architectural materials.

Understanding the rate of building material deterioration over centuries is challenging but vital. Analyzing monument deterioration rates in urban and rural settings highlights the significant influence of urban air pollution on architectural materials.

The relationship between air pollution and its adverse environmental consequences is complex. Despite decreases in harmful primary pollutants since the early 20th century, ongoing building and monument degradation persist due to ozone, nitrogen oxides, and photochemical smog.

SO_2, a prominent air pollutant, has been extensively studied for its effects on stone and commonly affects historical structures. Airborne contaminants have three primary effects on stone: chemical degradation, soiling or darkening, and aesthetic concerns, primarily reliant on dry deposition of SO_2 and subsequent conversion into sulphate by oxidation.

Stones containing carbonate are particularly vulnerable to pollution, developing resilient gypsum outer layers in high SO_2 concentrations. Calcareous sandstones are susceptible to erosion due to atmospheric sulfuric acid corrosion. Despite granite's longevity and resistance to acidic pollutants, it can develop gypsum crusts and layers of clay-calcitic materials.

Recent declines in acidic pollutants have led to increased concerns regarding the darkening or soiling of building materials, necessitating greater aesthetic focus. Particulate matter buildup, especially carbonaceous particles, contributes to surface darkening over time.

Author Contribution Declaration

Abhishek Singh: Graphic Design, **Tanvir Arfin**: Writing-original draft, review, editing, proofreading and supervision, **Nikhila Mathew**: Literature survey, conceptualization and writing, **Abha Tirpude**: Literature survey, conceptualization and writing. All authors have read and agreed to the published version of the manuscript.

Data Availability Declaration

No new data was used for the research described in the article.

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