

# Effect of Atmospheric SO<sub>2</sub> and Acid Rain on Chemical Degradation of Cement-Based Materials

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**Abstract—** This project studies in detail the harmful effects of atmospheric sulfur dioxide (SO<sub>2</sub>) and acid rain on cement-based materials, which are widely used in construction activities such as buildings, bridges, and roads. These materials are continuously exposed to environmental conditions, especially in industrial and urban areas where pollution levels are significantly high. Among various pollutants, sulfur dioxide plays a major role in the formation of acid rain, which adversely affects the durability, strength, and overall performance of cement-based structures. The project further explains the chemical reactions involved in the formation of acid rain, where sulfur dioxide reacts with oxygen and water vapor present in the atmosphere to form sulfuric acid. This acid, when deposited on cement surfaces through rainfall, initiates a series of chemical reactions with important components of cement such as calcium hydroxide and calcium silicate compounds. These reactions lead to the formation of harmful products like gypsum and ettringite, which cause expansion, cracking, and gradual weakening of the material. In addition, this study describes the mechanism of degradation, including the penetration of acidic solutions into the pores of cement, internal stress development, and surface damage. The long-term effects include reduction in compressive strength, increased porosity, and structural instability of cement-based materials. Finally, the project also highlights various preventive measures to enhance durability, such as the use of sulfate-resistant cement, protective coatings, and control of environmental pollution. Overall, this study provides a clear understanding of the impact of acid rain on construction materials and suggests ways to improve their lifespan and performance.

**KeyWords-** Atmospheric SO<sub>2</sub>, Sulfur dioxide pollution, Acid rain, Cement-based materials, Concrete degradation, Chemical deterioration, Durability of concret.

## I. INTRODUCTION

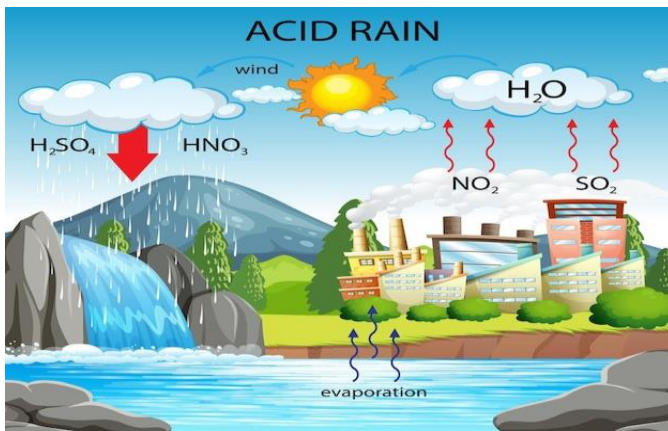
Cement-based materials, including concrete and mortar, are among the most widely used construction materials in the world. They form the fundamental components of infrastructure such as residential buildings, commercial complexes, bridges, highways, tunnels, and dams. Their popularity is mainly due to their high compressive strength, durability, adaptability to different shapes, and relatively low cost. These materials are designed to withstand various environmental and mechanical stresses over long periods of time.

However, despite their inherent strength and durability, cement-based materials are not completely immune to environmental degradation. In recent years, environmental pollution has emerged as a significant factor affecting the performance and lifespan of construction materials. Rapid industrialization, urbanization, and increased use of fossil fuels have led to the release of large amounts of harmful gases into the atmosphere. Among these pollutants, sulfur dioxide (SO<sub>2</sub>) is considered one of the most critical contributors to environmental

damage. Sulfur dioxide is primarily emitted from thermal power plants, petroleum refineries, industrial processes, and vehicular exhausts. Natural sources such as volcanic eruptions also contribute to SO<sub>2</sub> emissions, although to a lesser extent compared to anthropogenic sources. In densely populated and industrial regions, the concentration of SO<sub>2</sub> in the atmosphere can reach levels that significantly influence atmospheric chemistry. One of the most important consequences of increased SO<sub>2</sub> concentration is the formation of acid rain. Acid rain is a type of precipitation that contains acidic components such as sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and nitric acid (HNO<sub>3</sub>). The formation of acid rain involves a series of complex chemical reactions occurring in the atmosphere. Initially, sulfur dioxide reacts with oxygen to form sulfur trioxide (SO<sub>3</sub>). This sulfur trioxide further reacts with water vapor present in the atmosphere to produce sulfuric acid. This acid dissolves in cloud droplets and eventually falls to the ground as acid rain. The pH of normal rainwater is approximately 5.6 due to the presence of dissolved carbon dioxide forming weak carbonic acid. However, in the case of acid rain, the pH can drop to as low as 4 or even 3 in highly polluted areas. This increased

acidity makes rainwater highly reactive and capable of damaging natural as well as man-made materials.

When acid rain comes into contact with cement-based materials, it initiates a series of chemical reactions that lead to their gradual deterioration. Cement contains several compounds, including calcium silicates, calcium aluminates, and calcium hydroxide. Among these, calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) is particularly vulnerable to acid attack. The acidic components of acid rain react with calcium hydroxide to form calcium sulfate ( $\text{CaSO}_4$ ), which subsequently converts into gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).



#### 1. Emission Stage

$\text{SO}_2$  is released from industries, power plants, and vehicles into the atmosphere.

#### 2. Oxidation Stage

$\text{SO}_2$  reacts with oxygen ( $\text{O}_2$ ) to form sulfur trioxide ( $\text{SO}_3$ ).

#### 3. Hydration Stage

$\text{SO}_3$  reacts with water vapor ( $\text{H}_2\text{O}$ ) to produce sulfuric acid ( $\text{H}_2\text{SO}_4$ ).

#### 4. Cloud Formation

The acid mixes with cloud droplets.

#### 5. Precipitation

Acidic water falls as acid rain, affecting buildings, soil, and water bodies.

The formation of gypsum within the concrete structure leads to an increase in volume, which generates internal stresses. These stresses result in the development of cracks and micro-cracks within the material. Additionally, another compound known as ettringite may form under certain conditions. Ettringite

formation is also associated with expansion and contributes further to structural damage.

The degradation process is not limited to surface reactions. Due to the porous nature of concrete, acidic solutions can penetrate deep into the material through capillary pores and micro-cracks. This allows the chemical reactions to occur not only on the surface but also within the internal structure of the material. Over time, continuous exposure to acid rain leads to significant loss of strength, increased porosity, reduction in density, and overall deterioration of mechanical properties.

Another important aspect of acid attack is leaching, where essential components such as calcium ions are removed from the cement matrix. This process weakens the binding structure of the material, making it more susceptible to further damage. As a result, the structural integrity of buildings and other constructions is compromised, leading to safety concerns and increased maintenance costs.

In addition to structural damage, acid rain also affects the aesthetic appearance of buildings. Surface discoloration, roughness, and erosion reduce the visual appeal of structures, especially in monuments and heritage sites. This has been observed in many historical structures around the world, where prolonged exposure to polluted environments has caused significant damage.

The problem of acid rain and its impact on cement-based materials is particularly severe in developing countries, where rapid industrial growth is often accompanied by insufficient environmental regulations. Therefore, understanding the interaction between atmospheric pollutants and construction materials has become essential for sustainable development.

To address this issue, researchers and engineers are focusing on developing materials and techniques that can resist acid attack. These include the use of sulfate-resistant cement, incorporation of supplementary cementitious materials such as fly ash and silica fume, and application of protective coatings on concrete surfaces. Additionally, controlling  $\text{SO}_2$  emissions through environmental policies and cleaner technologies is crucial for reducing the occurrence of acid rain.

In conclusion, the study of the effects of atmospheric sulfur dioxide and acid rain on cement-based materials is of great importance in the field of civil engineering and environmental chemistry. A thorough understanding of the chemical reactions, degradation mechanisms, and preventive strategies is necessary to enhance the durability, safety, and sustainability of modern infrastructure.

## II. LITERATURE REVIEW

The impact of atmospheric sulfur dioxide ( $\text{SO}_2$ ) and acid rain on cement-based materials has been extensively studied by researchers over the past several decades. Early studies primarily focused on the general effects of environmental pollution on construction materials, while recent investigations have provided a deeper understanding of the chemical and physical mechanisms responsible for the degradation of cement and concrete structures.

One of the fundamental findings reported in the literature is that acid rain, primarily composed of sulfuric acid ( $\text{H}_2\text{SO}_4$ ), reacts readily with the alkaline components of cement. Cement-based materials are inherently alkaline in nature due to the presence of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), which is formed during the hydration of cement. This compound plays a crucial role in maintaining the stability and strength of concrete; however, it is highly susceptible to acid attack.



Several researchers have demonstrated that when acid rain comes into contact with cement surfaces, a neutralization reaction occurs between sulfuric acid and calcium hydroxide. This reaction leads to the formation of calcium sulfate ( $\text{CaSO}_4$ ), which further combines with water to form gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The formation of gypsum is one of the primary causes of deterioration in cement-based materials, as it alters the internal structure and reduces the binding properties of the material.

In addition to gypsum formation, the literature also highlights the formation of ettringite, a complex calcium sulfoaluminate hydrate. Ettringite formation occurs when sulfate ions penetrate the cement matrix and react with calcium aluminate phases. This process results in significant expansion within the concrete, leading to internal stresses, cracking, and eventual

structural failure. Many studies have identified ettringite formation as a major factor responsible for sulfate attack in concrete structures.

Research conducted over the last decade (2015–2024) has emphasized the role of environmental conditions in accelerating the degradation process. It has been observed that structures located in industrial and urban areas are more vulnerable to acid attack due to higher concentrations of atmospheric pollutants. High humidity, temperature fluctuations, and the presence of other acidic gases such as nitrogen oxides ( $\text{NO}_x$ ) further enhance the rate of chemical reactions, leading to faster deterioration.

Another important aspect discussed in the literature is the role of porosity and permeability of concrete. Highly porous materials allow easier penetration of acidic solutions into the internal structure, thereby increasing the extent of damage. Studies have shown that concrete with lower water-cement ratio and higher density exhibits better resistance to acid attack, as it restricts the movement of aggressive ions within the matrix.

Furthermore, long-term experimental studies have revealed that continuous exposure to acid rain results in a gradual reduction in compressive strength and durability of cement-based materials. Surface erosion, scaling, and leaching of calcium ions are commonly observed phenomena. The leaching process removes essential components from the cement matrix, weakening the overall structure and making it more susceptible to further environmental damage.

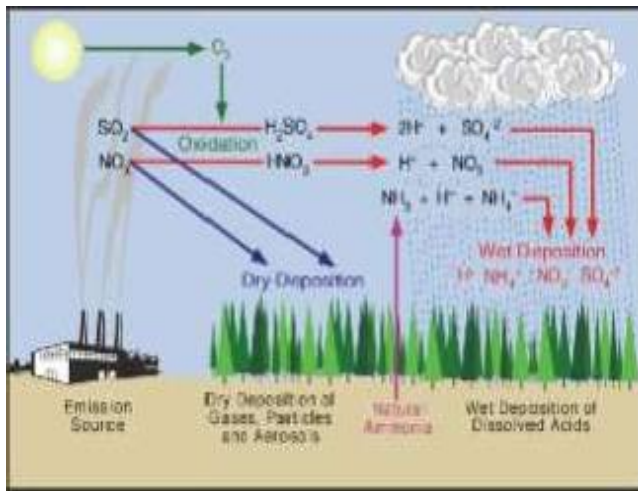
Several researchers have also focused on the microstructural changes occurring in cement under acid attack. Advanced techniques such as scanning electron microscopy (SEM) and X-ray diffraction (XRD) have been used to analyze the formation of degradation products like gypsum and ettringite. These studies provide clear evidence of structural changes at the microscopic level, which ultimately affect the macroscopic properties of the material.

In addition to experimental studies, field investigations have been carried out on real-life structures exposed to polluted environments. Observations from bridges, buildings, and historical monuments indicate that acid rain causes visible damage such as surface roughness, discoloration, and cracking. These findings support laboratory results and highlight the practical significance of the problem.

Recent literature also explores the development of materials and techniques to improve the resistance of cement-based

materials to acid attack. The use of supplementary cementitious materials such as fly ash, silica fume, and slag has been found to enhance durability by reducing porosity and improving the microstructure. Additionally, the application of protective coatings and sealants can prevent the direct contact of acidic solutions with the concrete surface.

Moreover, modern research is focusing on innovative solutions such as self-healing concrete and nano-materials, which have the potential to repair cracks and improve resistance against chemical attacks. These advancements indicate a growing interest in sustainable construction practices and long-lasting materials.



Despite significant progress, the literature identifies certain research gaps. Most studies are conducted under controlled laboratory conditions, which may not fully represent real environmental scenarios. There is a need for more long-term field studies to understand the combined effects of multiple environmental factors. Additionally, the development of cost-effective and environmentally friendly protective measures remains a challenge.

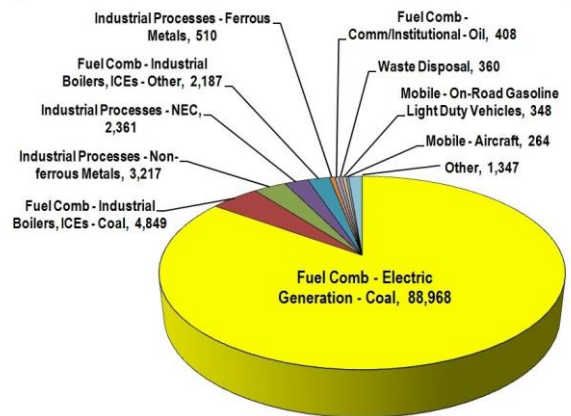
In conclusion, the existing literature clearly establishes that acid rain has a detrimental effect on cement-based materials through chemical reactions that lead to the formation of gypsum and ettringite. These processes cause expansion, cracking, and loss of structural integrity. The findings of previous studies provide a strong foundation for understanding the degradation mechanisms and highlight the importance of adopting preventive strategies to enhance the durability of construction materials.

**Sources of Atmospheric SO<sub>2</sub>**

Atmospheric sulfur dioxide (SO<sub>2</sub>) is a significant air pollutant that originates from a wide range of natural as well as anthropogenic (human-induced) sources. It plays a crucial role in atmospheric chemistry and is one of the primary contributors to environmental problems such as acid rain and air pollution. Understanding the sources of SO<sub>2</sub> is essential for controlling its emission and minimizing its harmful effects on both the environment and construction materials.

Natural sources of sulfur dioxide include volcanic eruptions, geothermal activities, and the natural decomposition of organic matter. Volcanic eruptions release large quantities of SO<sub>2</sub> directly into the atmosphere, which can travel long distances and influence atmospheric conditions on a global scale. Similarly, geothermal vents and hot springs emit sulfur-containing gases due to the interaction of underground heat with sulfur-rich minerals. In addition, the decay of organic materials in wetlands, oceans, and soil also produces small amounts of sulfur compounds that may eventually convert into SO<sub>2</sub>. Although these natural sources contribute to the overall sulfur cycle, their impact is generally less significant compared to human activities.

**Top Sources in 7 County Area for SO<sub>2</sub> Emissions (104816 tons/year)**



The major contribution to atmospheric SO<sub>2</sub> comes from anthropogenic sources, particularly due to rapid industrialization and increased energy demand. The burning of fossil fuels such as coal and petroleum is the largest source of SO<sub>2</sub> emissions worldwide. Thermal power

plants that use coal as a primary fuel release large amounts of sulfur dioxide during combustion, as coal often contains sulfur impurities. Similarly, petroleum refineries and diesel-based industries emit SO<sub>2</sub> during fuel processing and usage.

Industrial activities such as metal smelting, cement manufacturing, and chemical production are also major sources of sulfur dioxide. In metal smelting processes, sulfide ores are heated to extract metals, releasing SO<sub>2</sub> as a by-product. These emissions are often concentrated in industrial zones, leading to high local pollution levels. Additionally, oil refineries release sulfur compounds during the refining of crude oil, contributing further to atmospheric SO<sub>2</sub>.

In urban and industrial regions, vehicular emissions also play a significant role in increasing SO<sub>2</sub> concentration. Although modern fuels are relatively low in sulfur content, the large number of vehicles on roads contributes cumulatively to air pollution. Diesel engines, in particular, are known to emit sulfur compounds, especially in areas where fuel quality regulations are not strictly enforced.

Another important aspect is the accumulation and dispersion of SO<sub>2</sub> in the atmosphere. Once released, sulfur dioxide can remain in the air for several days, during which it undergoes various chemical transformations. It can react with oxygen and water vapor to form sulfuric acid, which contributes to the formation of acid rain. Atmospheric conditions such as wind patterns, temperature, and humidity influence the distribution and concentration of SO<sub>2</sub>, making some regions more vulnerable than others.

Furthermore, continuous and uncontrolled emission of sulfur dioxide has become a major environmental concern. High concentrations of SO<sub>2</sub> not only contribute to acid rain but also affect human health, causing respiratory problems and irritation of the eyes and throat. In addition, SO<sub>2</sub> plays a significant role in the degradation of building materials, particularly cement-based structures, by initiating chemical reactions that weaken their structural integrity.

In conclusion, atmospheric sulfur dioxide originates from a combination of natural and human activities, with anthropogenic sources being the dominant contributors. Effective control measures such as the use of low-sulfur fuels, installation of scrubbers in industries, and strict environmental regulations are necessary to reduce SO<sub>2</sub> emissions and minimize their harmful effects on the environment and infrastructure.

### Formation of Acid Rain

Acid rain is a serious environmental phenomenon that occurs as a result of complex atmospheric chemical reactions involving sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>). These gases are released into the atmosphere mainly from industrial activities, power plants, and vehicular emissions.

Once present in the atmosphere, they undergo a series of physical and chemical transformations that ultimately lead to the formation of acidic compounds.

The formation of acid rain begins when sulfur dioxide (SO<sub>2</sub>) is emitted into the atmosphere. This gas undergoes oxidation in the presence of atmospheric oxygen (O<sub>2</sub>), forming sulfur trioxide (SO<sub>3</sub>). This process may occur through direct reaction or with the help of catalysts such as particulate matter present in polluted air. In addition to sulfur dioxide, nitrogen oxides (NO and NO<sub>2</sub>) also contribute to acid rain formation by producing nitric acid (HNO<sub>3</sub>).

Once sulfur trioxide is formed, it reacts readily with water vapor (H<sub>2</sub>O) present in the atmosphere to produce sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). This acid is highly soluble in water and gets dissolved in tiny water droplets present in clouds. These droplets act as carriers of acidic substances and eventually combine to form precipitation in the form of rain, snow, or fog. When this precipitation reaches the earth's surface, it is referred to as acid rain.

The chemical reactions involved in this process can be summarized as follows:  $SO_2 + H_2O \rightarrow H_2SO_3$   
 $2SO_2 + O_2 \rightarrow 2SO_3$   $SO_3 + H_2O \rightarrow H_2SO_4$

Similarly, nitrogen oxides form nitric acid:  
 $NO_2 + H_2O \rightarrow HNO_3$

The acidity of rainwater is measured in terms of pH. Under normal conditions, rainwater has a pH of about 5.6 due to the presence of dissolved carbon dioxide forming weak carbonic acid. However, in polluted environments, the pH of rainwater can decrease to as low as 3–4, making it strongly acidic and highly corrosive in nature.

Acid rain can be classified into two types: wet deposition and dry deposition. Wet deposition occurs when acidic substances are dissolved in precipitation such as rain, snow, or sleet. Dry deposition, on the other hand, involves the settling of acidic particles and gases on surfaces, which later react with moisture to form acids. Both forms contribute significantly to environmental damage.

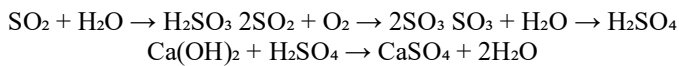
The effects of acid rain are widespread and severe. It can lead to the depletion of essential nutrients in soil, making it less fertile for agricultural purposes. In aquatic systems, acid rain lowers the pH of lakes and rivers, adversely affecting fish and other aquatic organisms.

Vegetation is also damaged due to the loss of essential minerals and direct injury to leaves.

Moreover, acid rain has a significant impact on construction materials, particularly cement-based structures. The acidic components react with the alkaline constituents of cement, leading to chemical degradation, loss of strength, and reduced durability. Buildings, monuments, and infrastructure exposed to acid rain show signs of erosion, discoloration, and structural damage over time.

In conclusion, the formation of acid rain is a complex process involving atmospheric reactions of sulfur dioxide and nitrogen oxides. Its highly acidic nature makes it a major environmental and structural hazard, emphasizing the need for controlling emissions and adopting sustainable practices to minimize its impact.

#### Chemical Reactions



### III. COMPOSITION OF CEMENT-BASED MATERIALS)

Cement-based materials, such as concrete and mortar, are complex composite systems primarily composed of various calcium compounds that play a crucial role in providing strength and durability. The main constituents of cement include calcium silicates, calcium aluminates, calcium hydroxide, and calcium sulfate. Each of these components contributes differently to the physical and chemical properties of cement.

The most important components of cement are calcium silicates, namely tricalcium silicate ( $\text{C}_3\text{S}$ ) and dicalcium silicate ( $\text{C}_2\text{S}$ ). These compounds are responsible for the development of strength in cement. Tricalcium silicate reacts rapidly with water during the early stages of hydration, providing initial strength to the structure, whereas dicalcium silicate reacts more slowly and contributes to long-term strength and durability. Together, these silicates form calcium silicate hydrate (C-S-H) gel, which acts as the primary binding material in concrete.

Another important constituent is calcium aluminate ( $\text{C}_3\text{A}$ ), which plays a significant role in the setting process of cement. It reacts quickly with water and contributes to the early stiffening of the cement paste. However, this compound is also highly reactive with sulfate ions, which can lead to the formation of ettringite under certain conditions, causing expansion and potential damage in cement structures.

Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), also known as portlandite, is formed as a by-product during the hydration of calcium silicates. Although it contributes to maintaining the alkaline nature of cement, it is relatively weak and highly susceptible to chemical attack. This compound is particularly vulnerable to acidic substances such as sulfuric acid present in acid rain. When calcium hydroxide reacts with acids, it leads to the formation of soluble salts, weakening the overall structure of the material.

Calcium sulfate is added to cement in the form of gypsum to control the setting time. It regulates the rapid reaction of calcium aluminate, preventing flash setting and ensuring proper workability of cement paste. However, under prolonged exposure to sulfate-rich environments, it can also participate in chemical reactions that may contribute to degradation.

During the hydration process, these compounds react with water to form a complex and dense microstructure consisting of calcium silicate hydrate gel and other crystalline products. This hydrated matrix provides mechanical strength, cohesion, and durability to cement-based materials. The structure formed is highly dependent on factors such as water-cement ratio, curing conditions, and composition of cement.

Despite the formation of a strong binding matrix, the presence of calcium hydroxide makes cement-based materials vulnerable to acid attack. Acidic solutions can easily react with  $\text{Ca}(\text{OH})_2$ , leading to its dissolution and removal from the matrix. This process, known as leaching, results in increased porosity and reduction in structural integrity. Over time, this degradation weakens the material and reduces its resistance to external environmental conditions.

In conclusion, the composition of cement-based materials is a balance of various chemical compounds that collectively provide strength and durability. However, certain components, especially calcium hydroxide, are highly reactive and make the material susceptible to chemical degradation, particularly under acidic conditions such as exposure to acid rain.

### IV. MECHANISM OF CHEMICAL DEGRADATION

The degradation of cement-based materials due to acid rain is a complex, multi-stage physico-chemical process that involves the interaction of acidic solutions with the hydrated cement matrix. This process does not occur instantly but progresses gradually over time through a sequence of well-defined steps.

Each stage contributes to the weakening of the material and ultimately leads to structural failure.

### 1. Penetration of Acidic Solution into Pores

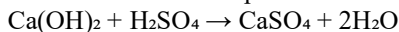
Cement-based materials such as concrete possess a porous microstructure consisting of capillary pores, gel pores, and micro-cracks. When acid rain comes into contact with the surface, the acidic solution begins to penetrate into these pores through capillary action. The rate of penetration depends on factors such as porosity, permeability, water-cement ratio, and curing conditions.

Highly porous concrete allows deeper and faster ingress of acidic solutions, increasing the exposure of internal components to chemical attack. Environmental conditions such as temperature and humidity further influence the penetration process. This stage is critical because it determines the extent to which the internal structure will be affected.

### 2. Chemical Reaction with Cement Components

Once the acidic solution penetrates into the cement matrix, it reacts with the alkaline components present in the hydrated cement. The most reactive compound is calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), which readily reacts with sulfuric acid ( $\text{H}_2\text{SO}_4$ ) present in acid rain.

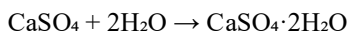
The reaction can be represented as:



This neutralization reaction leads to the dissolution of calcium hydroxide, which plays an important role in maintaining the alkalinity and stability of cement. The removal of  $\text{Ca}(\text{OH})_2$  weakens the cement matrix and initiates the degradation process. In addition, calcium silicate hydrate (C-S-H), the main binding phase, may also undergo decomposition under prolonged acidic exposure.

### 3. Formation of Gypsum and Ettringite

The calcium sulfate ( $\text{CaSO}_4$ ) formed during the reaction further reacts with water to produce gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Gypsum is a relatively soft and weak compound that does not contribute to structural strength.



Simultaneously, sulfate ions may react with calcium aluminate phases present in cement to form ettringite, a complex crystalline compound. The formation of ettringite involves the incorporation of water molecules and leads to a significant increase in volume.

Both gypsum and ettringite formation are critical stages in the degradation process, as they alter the internal microstructure and reduce the cohesive strength of the material.

### 4. Expansion and Internal Stress Development

The formation of gypsum and ettringite is accompanied by an increase in volume within the cement matrix. This expansion generates internal stresses because the surrounding material restricts free expansion. As a result, tensile stresses develop within the structure.

Concrete is strong in compression but weak in tension; therefore, the development of tensile stresses leads to the initiation of micro-cracks. Over time, these stresses accumulate and propagate, causing significant damage to the internal structure.

### 5. Crack Formation and Surface Damage

As internal stresses exceed the tensile strength of the material, cracks begin to form and propagate. Initially, micro-cracks develop at the microscopic level, but with continued exposure, these cracks widen and become visible on the surface.

Surface damage includes scaling, spalling, and erosion of the outer layer of concrete. The damaged surface becomes more permeable, allowing further ingress of acidic solutions, which accelerates the degradation process. This creates a cyclic effect where damage leads to more exposure, and more exposure leads to further damage.

### 6. Leaching and Loss of Material Integrity

Another important aspect of chemical degradation is leaching, where soluble compounds such as calcium ions are washed out from the cement matrix. This process reduces the density and cohesion of the material, making it weaker and more porous.

Leaching also results in the breakdown of the calcium silicate hydrate (C-S-H) gel, which is responsible for the strength of cement. The loss of this binding phase significantly reduces the load-bearing capacity of the structure.

### 7. Progressive Deterioration and Structural Failure

Over time, the combined effects of chemical reactions, expansion, cracking, and leaching lead to progressive deterioration of cement-based materials. The mechanical properties such as compressive strength, tensile strength, and durability are significantly reduced.

In advanced stages, large cracks, surface disintegration, and structural instability may occur, making the structure unsafe for

use. This ultimately results in costly repairs or complete failure of the structure.

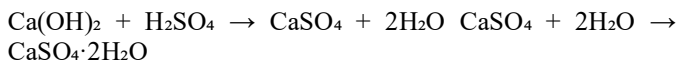
### Formation of Gypsum and Ettringite

The formation of gypsum and ettringite is one of the most critical processes responsible for the chemical deterioration of cement-based materials when exposed to acid rain or sulfate-rich environments. These compounds are produced as a result of chemical reactions between acidic or sulfate ions and the hydrated components of cement, leading to significant changes in the microstructure and mechanical properties of the material.

#### Formation of Gypsum

Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is formed when sulfuric acid ( $\text{H}_2\text{SO}_4$ ), present in acid rain, reacts with calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), which is a major hydration product of cement. This reaction is a neutralization process that results in the formation of calcium sulfate ( $\text{CaSO}_4$ ), which further combines with water molecules to form gypsum.

The chemical reactions involved are:



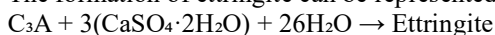
Gypsum is a relatively soft and less cohesive compound compared to the original cement matrix. Its formation leads to a reduction in the binding strength of concrete. Additionally, gypsum is slightly soluble in water, which can result in its gradual removal from the structure, increasing porosity and weakening the material further.

The accumulation of gypsum within the pores of concrete also alters the internal structure, making it more vulnerable to further chemical attack. Over time, this results in surface softening, scaling, and loss of material.

#### Formation of Ettringite

Ettringite is a complex calcium sulfoaluminate hydrate that forms when sulfate ions react with calcium aluminate phases ( $\text{C}_3\text{A}$ ) present in cement. This reaction generally occurs in the presence of water and leads to the formation of needle-like crystalline structures.

The formation of ettringite can be represented as:



Ettringite occupies a significantly larger volume compared to the original compounds, which leads to expansion within the cement matrix. This expansion generates internal stresses, as the surrounding material restricts the growth of ettringite crystals.

### Impact of Gypsum and Ettringite Formation

The combined formation of gypsum and ettringite plays a major role in the deterioration of cement-based materials. Gypsum weakens the matrix by reducing cohesion, while ettringite

causes expansion and internal stress. The pressure generated due to expansion leads to the development of micro-cracks, which gradually propagate into larger cracks.

As cracking increases, the permeability of the material also increases, allowing more acidic or sulfate-rich solutions to penetrate deeper into the structure. This accelerates the degradation process, creating a cycle of continuous damage.

In advanced stages, surface spalling, disintegration, and loss of structural integrity may occur. The material becomes brittle and loses its load-bearing capacity, making the structure unsafe.

## V. EFFECTS ON PHYSICAL AND MECHANICAL PROPERTIES

Acid attack on cement-based materials results in significant deterioration of both physical and mechanical properties. These changes occur due to continuous chemical reactions between acidic substances and the constituents of cement, leading to gradual weakening of the structure. The effects are not limited to the surface but extend deep into the internal matrix, affecting the overall performance and durability of the material.

### 1. Reduction in Compressive Strength

One of the most critical effects of acid attack is the reduction in compressive strength. Cement-based materials derive their strength mainly from calcium silicate hydrate (C-S-H) gel, which acts as the primary binding phase. When acidic solutions react with cement components, especially calcium hydroxide, it leads to the breakdown of this binding structure. As a result, the material loses its ability to withstand compressive loads. Over time, this reduction in strength can make structures unsafe and prone to failure under normal service conditions.

### 2. Increase in Porosity

Acid attack also leads to a significant increase in porosity within the cement matrix. This occurs due to the dissolution and leaching of calcium compounds, which creates voids and enlarges existing pores. Increased porosity allows easier penetration of water, acids, and other harmful ions into the material, accelerating further degradation. This creates a self-sustaining cycle where increased porosity leads to more damage, and more damage further increases porosity.

### 3. Surface Erosion

Surface erosion is one of the most visible effects of acid attack. The outer layer of concrete gradually deteriorates due to the removal of cementitious material. This results in a rough, uneven, and weakened surface. Continuous exposure to acid rain can cause significant loss of material thickness, reducing the protective cover over reinforcement and making the structure more vulnerable to environmental damage.

### 4. Cracking and Spalling

The formation of gypsum and ettringite within the cement matrix leads to expansion, which generates internal stresses. Since concrete is weak in tension, these stresses result in the development of cracks. Initially, micro-cracks form within the structure, but with continued exposure, they widen and propagate.

Spalling occurs when pieces of concrete break off from the surface due to internal pressure and weakening of the material. This not only affects the structural integrity but also exposes the inner layers to further chemical attack, accelerating the deterioration process.

### 5. Loss of Durability

Durability refers to the ability of a material to resist environmental and chemical attack over time. Acid attack significantly reduces the durability of cement-based materials by weakening their internal structure, increasing permeability, and reducing resistance to external forces. As durability decreases, the lifespan of the structure is shortened, and the need for maintenance and repair increases.

## V. CASE STUDIES / REAL-LIFE EXAMPLES

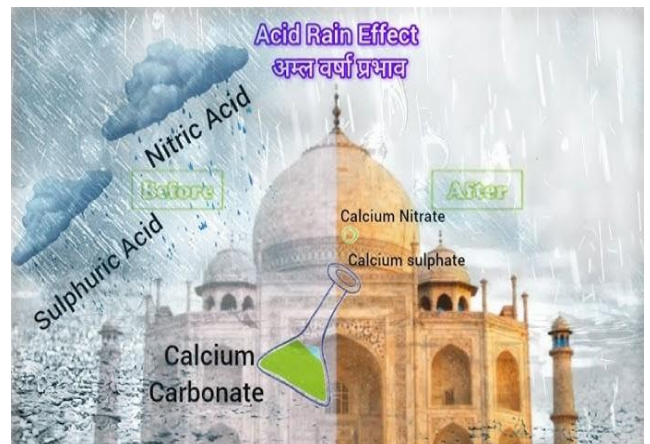
The impact of acid rain and atmospheric sulfur dioxide ( $\text{SO}_2$ ) on cement-based materials is not limited to laboratory studies; it is clearly visible in real-life structures across the world. Several case studies and field observations provide strong evidence of how acid rain contributes to the deterioration of buildings, monuments, and infrastructure. These examples help in understanding the practical significance of the problem and emphasize the need for preventive measures.

### 1. Taj Mahal (India): Damage Due to Acid Rain

One of the most well-known examples of acid rain damage is the Taj Mahal. This world-famous marble monument has been significantly affected by environmental pollution, particularly due to sulfur dioxide emissions from nearby industries and oil refineries.

The  $\text{SO}_2$  released into the atmosphere reacts to form acid rain, which falls on the surface of the Taj Mahal. Over time, this has caused discoloration of the white marble, turning it yellowish and dull. The chemical reactions between acid rain and calcium carbonate present in marble lead to the formation of gypsum, which weakens the surface.

In addition to discoloration, surface erosion and loss of smoothness have also been observed. This has raised serious concerns about the preservation of this historical monument, leading to the establishment of the Taj Trapezium Zone (TTZ) to control pollution in the surrounding area.



### 2. Industrial Regions: Faster Concrete Degradation

In heavily industrialized areas, the concentration of sulfur dioxide and other pollutants is significantly higher, leading to accelerated degradation of cement-based materials. Structures located near factories, power plants, and refineries are continuously exposed to acidic gases and particulate matter.

Field studies have shown that concrete structures in such regions experience faster chemical degradation due to continuous exposure to acid rain and dry deposition of pollutants. The formation of gypsum and ettringite within the concrete matrix leads to expansion, cracking, and reduction in strength.

For example, buildings near thermal power plants often show visible signs of damage such as surface scaling, cracking, and reduced durability within a shorter time span compared to structures in less polluted areas. This demonstrates the direct relationship between pollution levels and the rate of material degradation.

### 3. Bridges and Flyovers: Structural Weakening

Bridges and flyovers are critical infrastructure components that are constantly exposed to environmental conditions, including acid rain. In urban areas with high traffic and industrial emissions, these structures are particularly vulnerable to chemical attack.

The acidic components present in rainwater penetrate the concrete surface and react with cement constituents, leading to internal damage. Over time, this results in cracking, spalling, and corrosion of reinforcement bars (steel). The corrosion of steel further expands and creates internal pressure, worsening the damage.

Several studies have reported reduced load-bearing capacity and increased maintenance requirements for bridges exposed to polluted environments. In extreme cases, structural safety may be compromised, highlighting the importance of regular inspection and preventive measures.

### 4. European Monuments: Surface Erosion Due to Pollution

Many historical monuments and buildings in Europe have also suffered significant damage due to acid rain. Structures made of limestone and marble are particularly vulnerable, as these materials react readily with acidic substances.

Monuments in cities like London, Rome, and Paris have shown clear signs of surface erosion, blackening, and loss of fine details due to prolonged exposure to polluted air. The reaction between acid rain and calcium carbonate leads to the formation of soluble compounds, which are washed away, causing gradual loss of material.

This has led to the deterioration of architectural details and artistic carvings, affecting the cultural and historical value of these monuments. Conservation efforts now include regular cleaning, protective coatings, and strict pollution control measures.

#### Preventive Measures

The deterioration of cement-based materials due to acid rain and sulfur dioxide exposure can be effectively minimized by adopting appropriate preventive measures. These measures focus on improving the resistance of materials, reducing environmental pollution, and ensuring proper maintenance of structures.

#### Use of Sulfate-Resistant Cement

One of the most effective methods to prevent chemical degradation is the use of sulfate-resistant cement. This type of cement contains a lower proportion of tricalcium aluminate

(C<sub>3</sub>A), which reduces its reactivity with sulfate ions. As a result, the formation of harmful compounds like ettringite is minimized, thereby enhancing the durability of concrete structures in aggressive environments.

#### Application of Protective Coatings

Protective coatings act as a barrier between the concrete surface and the external environment. Materials such as epoxy coatings, polymer-based sealants, and waterproof membranes are commonly used to prevent the penetration of acidic solutions. These coatings reduce permeability and protect the internal structure from chemical attack, thereby increasing the service life of the material.

#### Use of Pozzolanic Materials

The incorporation of pozzolanic materials such as fly ash, silica fume, and slag improves the microstructure of cement-based materials. These materials react with calcium hydroxide to form additional calcium silicate hydrate (C-S-H) gel, which enhances strength and reduces porosity. Lower porosity limits the ingress of harmful ions, making the material more resistant to acid attack.

#### Reduction of SO<sub>2</sub> Emissions

Controlling the emission of sulfur dioxide is a crucial step in reducing acid rain formation. This can be achieved through the use of cleaner fuels, installation of scrubbers in industrial plants, and implementation of strict environmental regulations. Adoption of renewable energy sources such as solar and wind power also helps in reducing dependence on fossil fuels and minimizing SO<sub>2</sub> emissions.

#### Regular Inspection and Maintenance

Regular monitoring and maintenance of structures are essential to detect early signs of damage such as cracks, surface erosion, and discoloration. Timely repair using suitable materials can prevent further deterioration. Maintenance practices such as sealing cracks and reapplying protective coatings significantly enhance the durability and safety of structures.

## VI. CONCLUSION

This study clearly demonstrates that atmospheric sulfur dioxide (SO<sub>2</sub>) and acid rain have a significant impact on the durability and performance of cement-based materials. The interaction of acidic components with cement leads to chemical reactions that result in the formation of gypsum and ettringite. These compounds cause expansion, internal stress, cracking, and gradual weakening of the structure.

The research highlights that the degradation process is progressive and affects both the physical and mechanical properties of materials. Factors such as porosity, environmental conditions, and composition of cement play an important role in determining the extent of damage.

Furthermore, the study emphasizes the importance of adopting preventive measures such as the use of sulfate-resistant cement, pozzolanic materials, and protective coatings. Equally important is the control of environmental pollution through the reduction of SO<sub>2</sub> emissions.

In conclusion, a combined approach involving material innovation, proper design, and environmental management is essential for achieving sustainable construction. Understanding the mechanisms of degradation and implementing appropriate solutions can significantly enhance the lifespan and safety of structures.

### Summary

This project provides a comprehensive understanding of the effects of sulfur dioxide and acid rain on cement-based materials. It begins by explaining the sources of SO<sub>2</sub> and the process of acid rain formation through atmospheric chemical reactions.

The study further describes the composition of cement and the chemical reactions involved when acidic substances interact with its components. Detailed explanations of degradation mechanisms, including gypsum and ettringite formation, are presented to illustrate how structural damage occurs over time.

In addition, the project discusses the impact of acid rain on physical and mechanical properties such as strength, porosity, and durability. Real-life examples and case studies are included to highlight the practical significance of the problem.

Finally, the study outlines various preventive measures and modern approaches to improve resistance against acid attack. Overall, this project emphasizes the importance of understanding environmental effects on construction materials and adopting sustainable practices to ensure long-lasting infrastructure.

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