
1

THE MANY FACES OF ATMOSPHERIC CORROSION

1.1 DR. VERNON'S LEGACY

Thousands of years ago, humanity wrested materials from beneath the surface of Earth and processed them into spear points, rudimentary tools, and ornamental objects, which immediately began to corrode and have been corroding ever since. As technology has evolved and our atmosphere has come to contain increasing levels of acid gases, the rates of corrosion have increased. Everyday corrosion claims its victims—electronic connectors, towering bridges, and unique statuary. The forces opposing these processes are composed of corrosion scientists and engineers, whose war plan must, of necessity, be based on anticipating, understanding, and overcoming the enemy.

The science of atmospheric corrosion—corrosion that occurs in materials exposed to the ambient air—is less than a century old. Beginning in the 1920s, W.H.J. Vernon in England began systematic experiments in atmospheric corrosion. Except for some increased sophistication in instrumentation, his experiments were very similar to those of today: he cleaned metal samples, exposed them to specific concentrations of gases, such as SO_2 and CO_2 , or to natural outdoor environments, and determined corrosion rates and the major corrosion products.

Vernon's work took place some 80 years ago. Werner Heisenberg was just inventing the uncertainty principle of quantum physics, the neutron was not yet discovered, polymer chemistry was barely thought of, continental drift was an unsupported speculation, and the DNA double helix would not be discovered for 30 years. Today, quantum physics is a mature specialty, insight into the atomic nucleus has resulted in the use of nuclear power, polymers are ubiquitous, Earth science has been revolutionized by plate tectonics, and biological scientists have sequenced the human genome. Meanwhile, Vernon's experiments are still cited in the corrosion science literature as

relevant, at least occasionally. What has caused atmospheric corrosion science to stagnate while other scientific fields were forging ahead in great leaps and bounds?

One answer is that other fields are conceptually more straightforward and more highly specialized, while atmospheric corrosion is enormously complex and interdisciplinary. To understand quantum physics, one only needs the atom, its nucleus, and its electrons, for DNA only the molecule, although characterized by a highly complex structure. For atmospheric corrosion, however, one needs to understand a degraded solid phase, a very thin and transitory liquid phase, and a changing gas phase all at once and all without the ability to monitor everything during the time in which corrosion is actually occurring.

A second answer is that many applied investigations in corrosion science have had as their main emphasis the determination of the corrosion rate of a given metal in a given atmospheric environment. In these investigations, the corrosion products formed are to be removed from the metal by some chemical stripping treatment. However, this procedure not only determines the rate by removing the corrosion products, it also removes all the information hidden in the corrosion products that could tell something of what was going on during the corrosion process.

A third answer is that atmospheric corrosion has not traditionally attracted scientists performing fundamental research. In contrast, during the last three–four decades, a substantial amount of fundamentally orientated work in corrosion science has been devoted to understanding the chemical composition and atomic structure of passive films. Both atmospheric corrosion and passivity are research fields with enormous economic consequences. Yet, the efforts made in passivity have far outnumbered the efforts made in atmospheric corrosion. The main reason is simple: it is easier to set up and perform a well-defined laboratory experiment for fundamental passivity studies than for fundamental atmospheric corrosion studies. The former only needs two phases, the passivating metal and the liquid environment, whereas the latter needs three phases, the solid material, the atmosphere and a thin liquid film in between, and a thorough understanding of an intricate and rapidly changing atmospheric chemical environment.

1.2 CONCEPTS AND CONSEQUENCES

Atmospheric corrosion is the result of interaction between a material—an object made of a metal, a calcareous stone, a glass, or a polymer or covered by paint—and its surrounding atmospheric environment. The mechanisms that govern the corrosion or degradation of these materials differ greatly. The scope of this book has therefore been limited to the atmospheric corrosion of metals and alloys, whereas other types of materials only will be discussed occasionally. As opposed to the situation when the material is immersed in a liquid, atmospheric corrosion occurs during unsheltered exposure to rain or in rain-sheltered exposure indoors or outdoors.

Most frequently, atmospheric corrosion is triggered by atmospheric humidity, which forms a very thin water layer on the object. Depending on the humidity conditions, the water layer exhibits different thicknesses, resulting in various forms of atmospheric corrosion. In dry atmospheric corrosion or dry oxidation, the water layer

is virtually absent. A common example of dry oxidation is the tarnishing of copper or silver, which can proceed without any humidity in the presence of reduced sulfur compounds. In damp atmospheric corrosion, humidity and traces of atmospheric pollutants result in a thin, mostly nonvisible, water layer. Wet atmospheric corrosion requires rain or other forms of bulk water together with atmospheric pollutants and results in a relatively thick water layer, often clearly visible to the eye.

The consequences of corrosion on our society are enormous. In the United States, for example, the total costs for all forms of corrosion have been estimated to be around 1000 US\$ per capita per year. A substantial part of that amount is due to atmospheric corrosion. To estimate the costs for repair of corrosion-induced failures of our infrastructure, including bridges, elevated highways, railway, or subway systems, is tedious but can be done with a certain accuracy. It is more difficult to estimate the costs of direct or indirect consequences caused by atmospheric corrosion of electronic components or systems and how these can affect the reliability of security systems, aircraft, automobiles, or industrial processes. It is likewise difficult to estimate costs related to the loss of our cultural heritage. International concern has increased over the last decades as it has become evident that acid deposition through rain, snow, fog, or dew has resulted in substantial deterioration of artistic and historic objects, including old buildings and structures of historic value, statues, monuments, and other cultural resources.

1.3 THE EVOLUTION OF A FIELD

Developments in our understanding of atmospheric corrosion have been closely linked with society's need to gain more information about a visibly important process. During the first decades of the twentieth century, systematic field exposure programs were implemented in the United Kingdom and the United States when it became obvious that commonly used metals, particularly steel, copper, zinc, and aluminum, suffered from corrosion when exposed in heavily polluted atmospheric environments. The environments were categorized into rural, marine, urban, and industrial, and it was recognized that the metals exhibited different corrosion behaviors in these environments. In the 1920s and 1930s Vernon performed his pioneering work that transformed the field from art to science. He investigated the effect of relative humidity in combination with SO_2 and discovered a rapid increase in atmospheric corrosion rates above a critical relative humidity.

In the decades to come, many important contributions were made by distinguished scientists, including U.R. Evans, J.L. Rosenfeld, and K. Barton, who, among others, could demonstrate the importance of electrochemical reactions in atmospheric corrosion. Further improvements were made by W. Feitknecht, who took into account the chemical properties of the solid products of the corrosion process. Electrochemical techniques thus became common tools for exploring the underlying mechanisms. The success was only partial, however, because of the obvious difficulties of reproducing the actual atmospheric exposure situation in an electrochemical cell in which the sample is completely immersed in an aqueous solution or covered by a relatively thick aqueous layer.

In the 1960s and 1970s, atmospheric corrosion effects on electronic components and equipment were recognized. One of the first observations was made in the electronics of American aircrafts in the Vietnam War, which were not adequately protected from the tropical conditions of high humidity and high chloride concentration. It was soon recognized that even very small amounts of corrosion effects, detectable only by highly sensitive analytical techniques, could have detrimental effects on the reliability of electronics. This coincided with the advent of surface analytical techniques such as Auger electron spectroscopy and X-ray photoelectron spectroscopy, capable of providing information on the chemical composition of the outermost atomic layers of a corroded material. A new set of tools was thus available for the understanding of atmospheric corrosion mechanisms. They were complementary to the electrochemical techniques and able to provide more specific chemical information.

As a result of the increasing concern of acid deposition effects in general and the deterioration of the cultural heritage of various countries in particular, several national and international exposure programs were implemented in the 1980s and 1990s. The emphasis in some of these programs was not only on actual corrosion rates but also on a broader characterization of pollutant levels in the atmospheric environments. Efforts were made to correlate corrosion effects with levels of atmospheric constituents, mostly with limited success. Some exposure programs were also broadened to cover both metals and nonmetals and to indoor and outdoor exposures.

In the 1990s and the first decade of the new millennium, the focus was partially altered to consider also environmental consequences of atmospheric corrosion. Driven by new legislations primarily in Europe, the principal question from now on was not only what the environment does to the material but also what the material does to the environment as a result of corrosion. The last two decades have also seen a significant development in analytical tools based on, for example, vibrational spectroscopy, which can provide quantitative and qualitative information on the corrosion effects of a material during ongoing corrosion conditions.

1.4 CONTROLLED LABORATORY ENVIRONMENTS

Through exposures of materials in field environments, characterized by many atmospheric constituents having the potential to influence the corrosion behavior, Vernon and others soon felt the need to perform complementary exposures in laboratory environments, characterized by synthetic air with only a limited selection of atmospheric constituents. In designing such experiments a number of criteria have to be fulfilled, for example, How can a laboratory exposure be designed to simulate exposure in a given field environment? Do the same corrosion mechanisms occur in both types of environments? What ratio is obtained between the corrosion rates obtained in the laboratory and in the field?

Laboratory environments are usually characterized by constant relative humidity, constant temperature, and the addition of one or a few gaseous corrodents. For reproducibility reasons one usually tries to limit the number of gases to a maximum of four. Experience has shown that the levels of gases included in the laboratory

environment should not be too high in comparison with the levels found in the field environments; otherwise the possibility exists of stimulating nonrealistic corrosion mechanisms. Earlier laboratory exposures frequently suffered from this problem. With the advent of new instrumental apparatuses, for example, measuring devices for continuous monitoring of levels of gases and permeation tubes for producing low and stable emission of gases, it is now possible to produce laboratory environments with almost the same gas concentrations as occurring in the field.

A further development has been the increased availability of experimental techniques that can be used to monitor under *in situ* conditions changes occurring on a metal surface in the laboratory environment, that is, during ongoing corrosion. As will be shown in later chapters, this greatly improves the possibilities of tracing the main processes responsible for atmospheric corrosion.

1.5 UNCONTROLLED FIELD ENVIRONMENTS

If laboratory environments represent the simplest form of atmospheric environment for corrosion studies, uncontrolled indoor environments definitively represent a higher level of complexity. An indoor environment is usually characterized by relatively constant humidity, temperature, and airflow conditions and also by a broad spectrum of gaseous and particulate constituents, mostly at moderate and relatively constant levels. The constituents may have been produced either outdoors or indoors. In the former case, the levels may be reduced during transport from the exterior to the interior environment because of absorption on walls or in air treatment or ventilation systems.

The experience gained so far from indoor studies is relatively limited. Nevertheless it appears that indoor corrosion effects normally can be explained by the presence of a large number of air constituents at low levels, rather than by a few dominant constituents.

Outdoor environments generally represent the most complex type of environment from an atmospheric corrosion point of view. They are characterized by diurnal variations in temperature and relative humidity, the presence of numerous gases and particles, strongly varying airflow rates, and seasonal variations in solar radiation, temperature, and precipitation, including rain, dew, fog, and snow.

Outdoor exposure programs in one form or another have been carried out during most of the twentieth century. One main result is that corrosion rates under outdoor exposures are strongly influenced by two dominant constituents, sulfur dioxide and chloride ions, in addition to the climatic factors humidity and temperature. Despite numerous attempts, the goal of predicting the corrosion effect of a given material in a given environment remains far from attainment. This is due to the difficulty of taking into account many complicating factors, including the extent of rain sheltering, airflow conditions, and solar radiation.

An important challenge is to predict future corrosion rates based on expected changes in air constituent levels. Whereas the emission of sulfur dioxide has decreased significantly in many urban areas of Europe and North America, the presence of other corrosion-stimulating pollutants, including nitrogen dioxide and ozone, still remains high.

In other parts of the world (e.g., parts of Asia, Africa, and Central and South America), the emission of many gases has increased to very high levels.

1.6 NEW APPROACHES TO ATMOSPHERIC CORROSION STUDIES

Over the last few decades, the new analytical techniques developed to study properties of solid surfaces, such as chemical composition, oxidation state, morphology, and electronic structure, have continued to increase and to improve in terms of resolution and sensitivity. Most techniques are based on photons, electrons, atoms, or ions as probing particles. The earlier surface probing techniques require high vacuum during their application. Their use is therefore restricted for *in situ* studies of a surface, that is, during ongoing corrosion. The more recent analytical techniques are both surface sensitive and able to provide information under *in situ* conditions. The most promising of these from an atmospheric corrosion point of view include atomic force microscopy, the quartz crystal microbalance, infrared reflection absorption spectroscopy, confocal Raman spectroscopy, and the Kelvin probe. It is anticipated that the number and variety of *in situ* techniques for probing surfaces will continue to increase.

In parallel with the increased availability of *in situ* information from corroding surfaces is the gradual availability of computer models for describing atmospheric corrosion. In the best circumstances these should include all of the most important physical, chemical, and other processes. At least two such models have been developed; they appear to describe the most important processes that occur during initial exposure of metals to laboratory environments.

1.7 AN OVERVIEW OF THIS BOOK

The intent in this book is to bring together the information from experimental and theoretical studies of atmospheric corrosion of primarily metallic materials in such a way that the current state of knowledge is presented to the reader in a pedagogically useful and technically accurate manner. We have not attempted to review all relevant work or to present a compendium of information. Rather, our intent is to guide the reader through the evidence leading to a consistent scientific picture of the atmospheric corrosion process.

To address this target, we begin by describing a framework for an understanding of atmospheric corrosion, followed by an overview of the atmospheric species responsible for the corrosion processes. Advanced stages of corrosion are described, and reaction sequences presented. Specific applications such as electronics and cultural artifacts are addressed, and the costs and dispersion of metals due to atmospheric corrosion are discussed. The book culminates with projections for the corrosion environments of the future. Individual materials and their corrosion susceptibilities are presented in a series of appendices.

In this complex field and in a changing world, much remains to be learned about the details of atmospheric corrosion processes. Much information is known, however, and its selective presentation constitutes the remainder of this book.