Perspectives on Bronze Sculpture Conservation

Modelling Copper and Bronze Corrosion

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Cover picture: Dancing girls ("Danserskor") by Carl Milles in front of the Museum of Art in Göteborg. The sculpture was cast in 1915 and placed outdoors 1952. Photo: Helena Strandberg, 1997.

Perspectives on Bronze Sculpture Conservation
Modelling Copper and Bronze Corrosion

Doctoral dissertation for the Ph. D. degree

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Abstract

This dissertation presents different perspectives on the conservation of bronze sculptures and copper objects in outdoor environments. The problem complex is described regarding values assigned to sculptures, the condition of objects, deterioration processes in outdoor environments, and principles for conservation interventions in a historical and a modern perspective. The emphasis, however, is laid on laboratory investigations of crucial factors in deterioration processes.

The role of trace amounts of SO_2, O_3, NO_2 and NaCl on the atmospheric corrosion of copper, bronze and patina compounds was investigated using on-line gas analysis, gravimetry, and different corrosion product characterization techniques. Laboratory studies showed good agreement with studies from the field.

It was found that a black cuprite patina (Cu_2O) formed on copper in humid atmospheres at very low concentrations of SO_2, while higher levels of SO_2 passivated the surface. Cuprite was also predominant after exposure in certain environments, e.g. at 70% RH in an atmosphere containing SO_2+O_3, or in pure air when NaCl was applied on copper. The combination of SO_2+NO_2 implied that large amounts of green cupric salts were mainly formed, though at higher humidity (90% RH). A novel corrosion product, $Cu_{2.5}(OH)SO_4 \cdot 2H_2O$, was found which is likely to be a metastable precursor in the sulfation of copper and bronze. It is indicated that aged bronze patina containing green copper hydroxy sulfates may be converted to hydroxy chlorides by sea-salt deposition, subsequently to be converted to soluble sulfates by SO_2 deposition resulting in dissolution of patina in rain-exposed areas.

This dissertation suggests that the ratio cuprite/cupric salts generally has increased during the last decades on copper and bronze exposed in outdoor environments, e.g. as a result of reduced SO_2 concentrations and increased acidity of precipitation. Thus, the expectation that copper and bronze turn "naturally" green, which was a pollution-induced aesthetic ideal developing during the early part of the industrial epoch, may not always be fulfilled nowadays. As a consequence, streaked and patchy appearances of old bronze sculptures are more common. Regarding sculpture conservation, maintenance plans are urgently needed, especially for new art works.

Key words: copper, bronze, sculpture, atmospheric corrosion, air-pollutants, deterioration, conservation

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Papers

This dissertation is primarily based on and supported by the work presented in the following papers. The papers will be referred to by their Roman numerals in the text.

I Structure of $Cu_{2.5}(OH)_3SO_4\cdot 2H_2O$; a novel corrosion product of copper.
H. Strandberg, V. Langer and L.-G. Johansson.
Acta Chem. Scand. 49 (1995) 5.

II Outdoor bronze sculptures - a conservation view on the examination of the state of preservation.
H. Strandberg, L.-G. Johansson and J. Rosvall.
in *ICOM Committee for Conservation, 11th Triennial Meeting*, Edinburgh, Sept. 1996 (James & James, London, 1996), ed. by J. Bridgland, Vol. 2, p. 894.

III The formation of black patina on copper in humid air containing traces of SO_2.
H. Strandberg and L.-G. Johansson.
J. Electrochem. Soc. 144 (1997) 81.

IV Role of O_3 in the atmospheric corrosion of copper in the presence of SO_2.
H. Strandberg and L.-G. Johansson.
J. Electrochem. Soc. 144 (1997) 2334. ~~In press.~~

V Some aspects of the atmospheric corrosion of copper in the presence of sodium chloride.
H. Strandberg and L.-G. Johansson.
J. Electrochem. ~~Accepted for publication.~~ Soc. 145 (1998) 1093

VI The atmospheric corrosion of statue bronzes exposed to SO_2 and NO_2.
H. Strandberg, L.-G. Johansson and O. Lindqvist.
Materials and Corrosion (1997) November or December issue. ~~Accepted for publication.~~

VII Reactions of copper patina compounds - I. Influence of some air pollutants.
H. Strandberg.
Atmospheric Environment. ~~Submitted for publication.~~ 32 (1998) 3511

VIII Reactions of copper patina compounds - II. Influence of sodium chloride in the presence of some air pollutants.
H. Strandberg.
Atmospheric Environment. ~~Submitted for publication.~~ 32 (1998) 3521

The following publications, also produced during the course of this work, are not included in the dissertation due to their character of reports, to overlapping with the papers above, or to my small contribution to the work.

i A laboratory study of the atmospheric corrosion of statue bronzes and copper.
H. Strandberg, L.-G. Johansson and O. Lindqvist.
Eurocare-Copal (EU316). Report, June 1990, Department of Inorganic Chemistry, Chalmers University of Technology and University of Gothenburg (1990).

ii Initial stages of copper corrosion in humid air containing SO_2 and NO_2.
P. Eriksson, L.-G. Johansson and H. Strandberg.
J. Electrochem. Soc. 140 (1993) 53-59.

iii Bronsskulpturer utomhus i Göteborg - en undersökning av bevarandetillståndet.
H. Strandberg and J. Rosvall.
Institute of Conservation, Göteborg University (1994) 1994:16.

iv Förstudie rörande ytskydd för utomhus bronsskulpturer.
H. Strandberg and O. Lindqvist.
Institutionen för Oorganisk Kemi, Göteborgs Universitet (1994) OOK 94:07.

v The effect of air-pollutants on cultural objects - laboratory investigations.
H. Strandberg and L.-G. Johansson.
Metal 95, Proc. of the International Conference on Metal Conservation, Semour-Auxois, France, 25-28 Sept. 1995. James & James Ltd, London (1997) pp. 83-85.

Preface

My first contact with the problem complex of outdoor bronze sculpture conservation took place when I finished my degree as a conservator at The Royal Academy of Fine Arts in Copenhagen, and decided to study this subject as my diploma work. There were some dimensions that especially made me interested in the field.

Outdoor bronze sculptures are part of the art that many people experience every day. Large monuments, highly erected symbols of man's power, emperors on horses, busts, meeting places, figures without pedestals close and inviting to touch, sensual sculptures, expressions of beauty and harmony, and modern abstract forms are placed in public spaces and embellish streets, yards, squares and parks. The art works and memorials may represent a variety of messages and the various values that may be assigned to the objects make the problem of preservation and conservation an interesting and complex task. I found myself to be ambivalent toward this problem and one of the challenges was to inquire why, and find my own point of view.

Presentation of art in public spaces may claim to reach all people living in towns. The sculptures are not just for a minority but inevitably touch everybody whether desired or not, and nobody can completely avoid being confronted. Outdoor art is, unlike indoor objects, not locked in a collection where the beholder may choose when to face and take part in an aesthetic experience. Instead, the beholder is rather defenceless against the outdoor art and its messages. Conservation measures, as well as new art objects placed outdoors, therefore often attract much attention among the public. Fast changes of a specific object may thus be disturbing and provoking to some people while others welcome conservation or restoration.

Indoor bronze sculptures are essentially preserved in their original and intended state, guarded and protected behind locked doors, while outdoor sculptures, placed in the rough and corrosive outdoor environment, do not at all receive the same protection. The question is wether the alterations that occur on outdoor art works would have been tolerated for any indoor piece of art. The exposed position outdoors seems to be a reason for disregarding this problem.

After studying the available literature concerning outdoor bronze sculpture conservation, my questions regarding these problems were still not answered sufficiently. This was in the middle of the 1980s, when attention had recently begun to be paid to the devastating air pollution situation, and the field of bronze sculpture conservation had just started to develop. There was a great lack of knowledge of the deterioration process and all the other problems connected with it, but research had been initiated at several places around the world.

Some years later when I was given the opportunity to do research within this field, at the Department of Inorganic Chemistry in Göteborg, it was a fate and a challenge I had to face. Since that time my work has greatly focused on the small world of molecules interacting with copper and bronze surfaces, and I have striven to understand some of the mysteries that arise. The fascination with methods of natural science is that they are a possible way to understand and model reality. Even if the causality relation is only valid for certain isolated conditions, extrapolation to the complex world is possible and some crucial factors in the deterioration process may thus be revealed. The long path of my work has resulted in the appended papers that hopefully make up a useful contribution to the accumulated knowledge within the field. Writing this dissertation, I take the opportunity to return to some of my original questions and try to integrate the laboratory studies into a context whose focus is upon the cultural objects.

This dissertation could not have been the same without the previous work that has been carried out within the field throughout the years. Therefore, I first of all would like to sincerely thank all these authors (see bibliography) for their research on which the dissertation and the papers are built. The information obtained by personal communication has also been an important source for this work (see unpublished references).

Even if most people that have been central for this dissertation have already been mentioned, there are some persons that especially should be acknowledged. Professor Oliver Lindqvist understands the need for cross-disciplinary research and gave me the opportunity to start working within the field, moreover he gave me the push (now I admit necessary) out of it. Lars-Gunnar Johansson has been my supervisor and has, by his impressive intuition for corrosion mechanisms and great understanding of chemical relations, guided me in the chemical world and has been helpful and generous in sharing his knowledge and world view. Jan Rosvall has encouraged and inspired me in my way of dealing with the problem of writing the dissertation, supervised me in the conservation field, and has been a fast and excellent reader. Vratislav Langer who has a sharp eye for crystals could patiently find a precious one. Urban Jelvestam and Ingemar Olefjord have showed their expertise in performing XPS, and Lars Eklund in using EPMA.

For financial support provided during my research, I would like to thank the Swedish Board of National Antiquities (RIK) and the Swedish National Board for Industrial and Technical Development (NUTEK). I also would like to acknowledge Outukompu Copper AB, RIK, and Institut für Silikatchemie und Archäometrie who have supplied some of the copper alloy material.

Siri Refsum gave me the opportunity to work with practical bronze sculpture conservation in the Vigeland Park in Oslo and has shared my deep interest in conservation of these artworks. I would like to express my thanks to Siri as well as to Liss Christenssen and other co-workers for interesting discussions, comments and suggestions, and for being pioneers in bronze sculpture conservation in Scandinavia. Also Jan Gullman and Mille Törnblom at RIK have a great knowledge of the problems of sculpture conservation and have contributed ideas and discussions. I gratefully acknowledge all the members of the Eurocare-Copal project for their presentations of work, aiming at conservation of copper alloys, at annual workshops in Europe. A special thank is expressed to Alfred Vendl and Bernhard Pichler who initiated the Copal-project, and I give my support to Martin Mach for continuing the coordination of this group.

I would like to thank members of the Department of Inorganic Chemistry, present and past, that are curious and inquiring of mind and have provided a creative atmosphere with a high level to the roof in laboratories, workrooms and corridors. These colleagues have also been of great support through these years, for understanding the necessity of hard and involved work, and for having insight that blood sweat and tears are needed for this process. Quick to rescue and practical assistance have been invaluable assets when capricious apparatus, computers and other technical equipment have been teasing me. I hope that all these persons not feel overlooked not being mentioned by names here.

The staff in the CTH library have showed great competence and fast helpfulness. Members of the Institute of Conservation have also been kind in supplying important literature.

Lastly, I would like to express my thankfullness for the fundamental necessities priceless for this period of my life. Thanks for love and play, for dance and music, for friendship, and for sharing values, difficulties, and the efforts in being mother and just a human being. Thanks for dinner in the evenings, fresh bread and a warm cup of tea in the mornings, clean laundry and clean dishes, a tidy home, newly ironed shirts, and for caring for a lovely child.

Göteborg, August 22, 1997

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Contents

Unpublished results

Appendix 1:

Some properties of copper patina compounds
Formation of $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$
XPS studies of copper hydroxy sulfates

Appendix 2:

A pilot study on the effects of air-pollutants on protective coatings for bronze sculptures

1 INTRODUCTION

1.1 The problem complex

Cultural objects, produced by man, may in the course of time deteriorate naturally. However, besides this natural decay, industrial society contributes large amounts of man-made factors that affect the process of deterioration. The ageing of cultural objects, as well as of other resources, may add quality if the outer conditions are favourable, and if the ageing proceeds with dignity, thus with care and maintenance as necessary aids. The predominant tendencies in the consumer society during the industrial epoch, though, have been neglect and waste of all kinds of resources.

Bronze sculptures in the corrosive outdoor environment alter with time in a way that may appear disfiguring for the objects. Patina of green and black areas, streaks and patches become prominent. The process of discoloration in outdoor atmosphere, however, is slow enough, such that the general population becomes used to the progressive change. The alterations take place in a very thin surface layer, but corrosion may nevertheless cause serious damage due to changes in the surface texture. Tool marks that are signatures of the artist and craftsman may be destroyed even if the corrosion rate is low. Form, colour and surface texture are essential for the perception of the sculpture and changes of these qualities may cause great loss of the aesthetic experience, the artistic expression and other kinds of information of value, but may also provide new dimensions to the sculpture. Regarding copper sheet metal on roofs and other architectural elements, the process of change continues in a similar way and is sometimes under certain conditions apprehended as desirable.

Many questions of diverse character have arisen when trying to understand the problem complex of bronze sculpture conservation, such as:

How would copper and bronze appear in an unpolluted outdoor atmosphere? How has the air pollution situation changed during the industrial epoch, and what changes in appearance and composition of the patina on outdoor objects have resulted? How long a time may pass before copper roofs turn green?

What is a desirable appearance of a patina? Should it be brown, green or black? Is it acceptable that sculptures become streaked or patchy? What are the expectations of the effect of time? Why do the apprehension and evaluation of the alterations of specific objects differ among groups of people and among individuals? Why has bronze sculpture conservation been much ignored?

Which kind of patina is protective on outdoor objects? What happens in the deterioration process? What corrosive species are crucial in the process and what changes occur in the patina layer? Which patina is stable in outdoor environments? Do compounds in the patina dissolve in the rain?

This dissertation is concerned with all these questions and deals with the problems on different levels of abstraction, ranging from values and significance that may be assigned to sculptures, to scientific investigations which concern deterioration processes, to the principles for direct conservation measures.

1.2 Aims and objectives

The *aim* of this dissertation is to study different perspectives on outdoor bronze sculpture conservation with the emphasis on investigating deterioration processes of copper and bronze. In this context, conservation is conceived as *a problem-oriented activity devoted to preserving natural, cultural and social resources in a process of change.*[1]

The objectives are:

– to view historical developments of conservation approaches and theories, and present measures performed concerning bronze sculpture conservation (section 2).

– to briefly present some material properties and the use of copper and bronze alloys (section 4).

– to characterize the state of preservation and present stages of deterioration of sculptures in outdoor environments (section 5 or Paper II).

– to sketch trends in the air pollution situation during the industrial epoch (section 6).

– to elucidate the influence of corrosive atmospheric species on copper, bronze, and patina compounds in order to understand crucial deterioration mechanisms occurring (section 7). Investigations have been performed by using controlled laboratory studies in synthetic atmospheres (Papers III-VIII).

– to characterize, in some specific cases, structural and physical properties of corrosion products present in patina layers (Paper I, Appendix 1).

– to discuss previous and present situations concerning deterioration mechanisms and propose actions and future needs concerning bronze sculpture conservation (sections 7-9).

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[1] Rosvall *et al.*, 1995. This is the expanded definition of conservation, a paradigm that may be applied to several types of domains.

1.3 Scope of the dissertation

The dissertation mainly deals with degradation processes on copper and bronze in corrosive atmospheres. It is based on eight appended papers that have been published or have been submitted for publication. The papers provide details of methods, results and extensive discussions. The main results from the appended papers support the dissertation and are integrated in a review of previous work within the field. The methodology used for achieving the results is presented in section 3.

1.4 Definition of concepts

Some concepts that are frequently used throughout the dissertation are defined below:

The word *patina* was printed, for the first time known, in 1681 in Baldinucci's art dictionary where it is defined as *"a term used by painters, called by others a skin, namely that general dark tone which time causes to appear on paintings, that can occasionally be flattering to them"*. In the French "Encyclopédie" from 1751 the word is used referring to the green corrosion products on copper and is defined as follows: *"There is no French word to express that beautiful and brilliant color of verdigris which copper does not always assume"*.[2]

In this dissertation a *patina* on a copper or bronze object is defined as *the result of the actions of the environment on the metal surface*. This wider definition does not evaluate whether the patina is desirable or not. All copper and bronze thus exhibit patina of varying properties, e.g. colour, morphology and composition. Besides corrosion products, deposited material such as soot, dust, sand, etc., and old surface treatment are also included in the definition.

The term *corrosion* is here defined as *the material's attack by, or reaction with, its environment*[3] *irrespective of whether the reaction is detrimental to the material or not*. The definition is not restricted to metals; consequently patina compounds and other materials (e.g. stone, paper, plastic, lacquers) may corrode as well.

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[2] Weil, 1977. Citations: *"Patena, voce usata da' 'Pittori, e diconla altrimenti pelle, ed è quella universale scurità che il tempo fa apparire sopra le pitture, che talvolta le favorisce."; and "Il n'y a point de mot françois pour exprimer cette belle & brilliante couleur de vert-de-gris que le cuivre ne prend pas toujours..."*

[3] In accordance with Fontana, 1987, p. 4; Shreir, 1963, p. 1.

2 AN OUTLINE OF THE HISTORY AND THEORY OF CONSERVATION

This survey first presents some of the most recognized and relevant approaches to conservation from various historical periods. The view of alterations of copper and bronze objects in the outdoor environment during the industrial epoch, and the concern for sculptures, are reviewed in a historical and a modern perspective as well as diverse approaches to conservation.

The theoretical framework of this dissertation is based on a system approach for identifying the problem complex regarding bronze sculpture conservation on different levels of abstraction.[4] The problem is described on the highest level of abstraction that concerns the values assigned to sculptures; on the normal scientific level where crucial deterioration processes are identified; and on the operational level where direct conservation measures are performed.

Finally, some approaches and performed measures in different countries within bronze sculpture conservation are described.

2.1 Historical development of conservation approaches

The *traditional approach* to conservation implies that historic structures were preserved if they continued to have use values. Maintenance measures and restoration interventions had the purpose of keeping the function intact.[5] The first known, consciously projected attempts to preserve and restore ancient monuments for culturally defined reasons were made during the Italian Renaissance. A change in attitude occurred due to the awakening interest in the classical periods, and the new appreciation of the monuments remaining from antiquity. Jokilehto defined this approach as *romantic restoration*.[6]

During the 19th century, with the evolution of nationalism and romanticism in Europe, consciously developed *stylistic restoration* first appeared in France. In the

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[4] For a presentation of a system approach and definition of important concepts, see van Gigch, 1991; and van Gigch *et al.*, 1996.

[5] Jokilehto, 1988.

[6] Riegl, 1982; Jokilehto, 1988; Feilden, 1988.

restoration of buildings new details were added in what were apprehended as appropriate styles.[7] Since architects often liked to leave memorials after themselves, restoration projects tended to lead to re-creation of buildings, with features representing the current period. Much of archaeological and historical value thereby was destroyed. According to Feilden[8] the stylistic revival can be seen as a way of escaping from the drastic changes created during the industrial revolution.

Contemporaneously, an *"anti-restoration"* movement developed as a reaction to the stylistic restoration. Historical consciousness among intellectuals and *"ruin romanticism"* that concerned the pure extrinsic love for ruins as symbols of change and decline, led to the demand for no intervention by man, aiming to avoid falsifying the intrinsic values of the monuments.[9] Authenticity in relation to the original object was emphasized in this *historical approach*, as reproduction of objects with the same significance in a different context was considered impossible.[10]

The last two of the above-presented approaches, which may be defined as *"restoration"* versus *"conservation"*, have since their birth resulted in many conflicts. In Italy, the debate on these issues came to a compromise at the end of the 19th century, and documentation was mutually emphasised. At the first international meeting, in Athens in 1931, a *modern conservation theory* was presented where the tendency was to avoid restoration and to favour conservation of the authenticity of historic monuments. Maintenance was recommended in order to ensure preservation. When restoration became indispensable, the work of art should be respected without excluding the style of any given period. The use of modern materials, e.g. concrete, was approved of.[11]

After the devastating destruction of cultural property during the Second World War the balance between scholarly-scientific and aesthetic aspects of conservation was shifted. Since the end of the 19th century, attention was primarily given to historic and documentary values, but in the rebuilding of Europe the tendency towards artistic and aesthetic aspects was stressed. The stylistic restoration was again discussed but became condemned.[12] An Italian doctrine gradually was developed, called *"restauro critico"*, in which both historic and comprehensive aesthetic values were recognized.[13]

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[7] Blomé, 1977; Feilden, 1988; Jokilehto, 1988.

[8] Feilden, 1991; Feilden, 1988.

[9] Blomé, 1977.

[10] Jokilehto, 1988. According to Jokilehto, 1995, *"authentic"* was defined in 1849 as something that is *"sufficient to itself, which commends, sustends, proves itself, and hath credit and authority from itself"*. Jokilehto assigns the use of the concept *"to be authentic"* to something original, real, genuine, specific, unique, sincere, creative, true or exceptional. The concept does not give a value per se, but should be understood as *"the condition of an object in relation to its specific qualities"*.

[11] Blomé, 1977; Jokilehto, 1988; Feilden, 1991.

[12] Jokilehto, 1988; Jokilehto, 1988; Feilden, 1988.

[13] Blomé, 1977.

In 1950 the organisation IIC (originally the International Institute for Conservation of Museum Objects) was founded by scholars, scientists and professionals mainly concerned with conservation of museum artefacts. According to Feilden,[14] this was the initiation of the phase of *scientific conservation.* ICCROM (International Center for the Study of the Preservation and the Restoration of Cultural Property) was later founded, in 1959, by United Nations and UNESCO, to promote scholarly-scientific conservation of cultural property. The scientific conservation primarily deals with the causes of decay, and is described by Feilden to be like medicine, an art aided by science which is based upon careful diagnosis of the causes of decay. As decay follows laws of nature it cannot be entirely prevented but can be slowed down.

A critical judgement of the historic and aesthetic aspects was reflected in the *Venice Charter* formulated in 1964. In this document the historic monument is considered to remain as a message from the past, a living witness, which it is our duty to hand down to future generations in full richness of its authenticity. The basic principle is the authenticity but the concept is not defined clearly. The process of restoration is defined as a highly specialised operation with the aim to preserve and reveal the aesthetic and historic value of the monument. The need for proper documentation before, during and after intervention is stressed. The Venice Charter has exercised an important influence all over the world during the past decades.[15]

The recent *Nara document* on authenticity, formulated in 1994,[16] was conceived in the spirit of the Venice Charter considering authenticity as the essential qualifying factor concerning values. The Nara document stresses that it is not possible to base judgements of value and authenticity on fixed criteria in our world of cultural diversity. On the contrary, as judgements about values may differ from culture to culture, and even within the same culture, authenticity should be considered and judged within the cultural contexts to which properties belong. In cases where values appear to be in conflict, respect for cultural diversity demands acknowledgement of the legitimacy of the cultural values of all parties. As a fundamental principle of UNESCO, responsibility for cultural heritage belongs, in first place, to the cultural community that has generated it, and subsequently, to that which cares for it. Knowledge and understanding of the values are assumed to be a requisite basis for assessing all aspects of authenticity.

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[14] Feilden, 1988; Feilden, 1991.

[15] Jokilehto, 1988; Feilden, 1988.

[16] Lemaire and Stovel, 1995. The conference held in Nara in Japan provided an in-depth analysis of the concept of authenticity; see Larsen, 1995.

2.2 The concern for bronze sculptures in a historical perspective

Weil has done extensive historical research on the approaches to patination and care of bronze sculptures. The first part of the following historical review is primarily based on some of her works.[17]

According to Weil, it appears to have been common practice to provide for regular maintenance of outdoor bronze statuary in ancient Greece and in some instances up to the Middle Ages. The gleaming burnished appearance of the metal itself was valued as the ideal state to be maintained. Pliny recommended polishing or rubbing with oil or protective varnish coatings of pine tar pitch to be regularly applied to preserve the surface from corrosion. He also described the use of bitumen, to give the same appearance to the bronze as to gilding. For cleaning bronze Pliny mentioned the use of vinegar and the urine of a child.

From antiquity until World War I some exceptions to the use of polished surfaces and glossy finishes are known. In late Roman antiquity, a dark patinated oxidation layer may have occurred on bronze sculptures, as well as coatings of wax, oil, or black lustrous lacquer. During the Renaissance, ancient bronzes were much admired. The corrosion products on the bronzes had acquired a value in themselves since they testified to age and therefore genuineness. Dark smoke patinas and lacquering in translucent red-browns were known at this time, and greening with acid was developed. During the 19th century, particularly in France, there was a development of artificial patination practised on a large scale. Artistic specialists, "patineurs", developed the art of colouring bronzes by application of heat and chemicals, and they carefully guarded their secrets. Small works were treated with great artistic skill and variety, while large works normally were given the simplest of treatments by chemicals to turn dark brown or black.

Before the industrial revolution, outdoor bronzes located far from chloride-containing sea-winds probably remained dark and lustrous, brown to black, occasionally tinged with green for a long time. Vernon[18] reported that copper spires in a remote part of Switzerland still were bright, except for yellow to rosy-red interference colours, after at least 30 years of exposure outdoors at the beginning of the 20th century. According to Weil, lustrous patina with the quality of "depth", caused by the reflection of golden metal through a thin dark layer of oxide, was much admired before the industrial epoch.

During the 1850s, concern was expressed in London for the effects of industrial pollution on paintings and stone exteriors. These complaints were mainly due to the accumulation of soot. Metal was also reported to corrode a hundred times faster in

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[17] Weil, 1977; Weil, 1980; Weil *et al.*, 1982.

[18] Vernon, 1932.

London than in the countryside.[19] The first alarm concerning outdoor bronze sculpture sounded in Berlin during the 1860s when changes regarded as both undesirable and unattractive were reported by Magnus.[20] He headed the Berlin Patina Commission and performed a number of extensive studies investigating nearly every aspect of problems of outdoor bronze preservation, ranging from technical examination including analysis of metal, corrosion products, and the influence of the composition of bronze on the formation of patina, to methods of treatment.

Magnus[21] reported that outdoor bronzes in Munich unfortunately were changing to become rough opaque black, giving the surface a dull appearance. The author also confirmed his observation by noticing the same change of the Berlin bronzes, and that all bronzes in London already had reached the stage of being black. The causes of formation of the black crust were related to sulfur compounds and carbon soot produced by the burning of fossil fuels in big towns. Magnus described the previous appearance of statues in towns as beautifully green still within living memory. Bronzes in gardens remote from cities principally remained green, and were reported not to change with time. The black crust, consisting of copper sulfur compounds, was supposed to impede the formation of an attractive green "malachite" patina.[22] Magnus also described a beautiful brown translucent patina on some of the protuberant parts of a postament, and proposed that it was caused by fat from hands touching the surface.

According to the observations above, the main concerns during the 19th century for bronzes were the black opaque copper sulfur deposits coloured by soot. The previously green appearance reported by Magnus did not cause any complaints. Considering that most outdoor sculptures even in the 19th century never were exposed in other than polluted air, the green appearance observed within living memory, as described by the author, probably also was a result of man-made air pollution. The properties of the actual green patina were not described, however, and the patina possibly had different characteristics than nowadays.

It may be noted that in Weil's review[23] of Magnus' works, including several references to Magnus, she described the change in appearance of outdoor bronzes from glossy and translucent to black, but did not mention the change from green. The word "green" was also excluded in the title of one of the references ("...einer schönen [grünen] Patina...").[24] Evidently, the conviction that the green patina was neither attractive nor protective did mislead the reviewer on this issue.

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[19] Brimblecombe and Rodhe, 1988.

[20] Magnus, 1864; Weil, 1980.

[21] Magnus, 1864.

[22] Vernon later reported this green patina to consist of basic copper sulfate, and not of malachite, see below.

[23] Weil, 1977; Weil, 1980; Weil *et al.*, 1982.

[24] Weil, 1980.

Magnus carried out some experiments which showed that frequent washing and rubbing with "bone oil" produced a handsome, lustrous patina, while simple washing did not promote a desirable patina. Other authors in Germany in the second half of the 19th century recommended cleaning solutions of alkalis or sulfuric acid. For protection and patination a mixture of vinegar and "bone oil" to produce a glossy translucent green patina was advised, to be polished on the bronze surface weekly. A protection by rubbing with oil or wax was also recommended.[25]

Regarding archaeological bronzes, chemical studies of ancient metals and corrosion products appeared during the period between 1800 and 1860 with the increased archaeological activity of Europeans in Egypt. This was followed by major studies on mechanisms of corrosion, analysis of corrosion products, durable alloys for casting, methods of patination, and protection of bronzes, especially in Germany. With this background, the first museum laboratory was established by Rathgen at the Berlin Museum towards the end of the century. This tradition of studies on bronzes ceased with World War I.[26]

The extensive German investigations and discoveries during the 19th century were later almost forgotten or ignored internationally. First in the 1920s Vernon[27] made important scientific studies and reported in England about the effects of atmospheric corrosion, obviously unaware of the German investigations. The author described the patina as "natural", "protective" and having "aesthetic value". He identified the green corrosion on copper roofs to be basic copper sulfate, and not the basic copper carbonate malachite as previously thought. The old misapprehension was probably due to the analysis of the green patina on archaeological bronzes consisting of basic copper carbonate.

Also Gettens,[28] who investigated a 35-year-old bronze statue in the 1930s, described the green patina under the black deposits as "quite harmless", "homogeneously formed as a substratum to the black layer", and as "probably having an aesthetic value". He suggested that the green patina was formed in the "early life" of the bronze when the soot and dust content was less in the air. However, the dull black deposit covering the green layer he ascribed to soot deposits from the increasing pollution, and he recommended that it be removed. Some bare green patches in the most exposed parts of the statue were observed where the black crust was washed away by rain water.

Most authors[29] of scientific and conservation literature during the 20th century accepted the pollution-induced corrosion as a "natural" phenomenon. Copper was much

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[25] Weil, 1980.

[26] Weil, 1980.

[27] Vernon and Whitby, 1929; Vernon, 1931; Vernon, 1932.

[28] Gettens, 1933, a statue in USA.

[29] See for example Vernon and Whitby, 1929; Vernon, 1931; Vernon, 1932; Mattsson and Holm, 1964; Mattsson and Holm, 1967.

used in architectural elements during the first part of the century, and artificial patination was used to rapidly acquire a green desirable "natural" appearance that also was assumed to be protective. E.g. the copper roof of the City Hall in Stockholm was manually patinated when it was laid in the beginning of the 1920s.[30] During the Art Deco period during the 1930s and 1940s the bright, dull (matt), opaque, green appearance of copper alloys even became a stylish vogue and was adopted by artists and architects.[31] The modernist influence reflected a new aesthetic ideal and the previous 19th-century tradition of patination was broken.[32] Vernon[33] worked out methods for rapid production of green artificial patina on copper and experimented with the application of protective coatings of linseed oil, lanolin, and even modern products such as water glass and silicon ester. During the 1960s, Mattsson and Holm[34] continued the research on green patination of copper roofs and the work led to a patented method, whereby an aqueous patina sludge containing chiefly copper nitrate was applied with a procedure that resembled painting. The pre-patinated copper material was used for prefabricated building components as new copper roofs and infill panels, and for the repair of old roofs, e.g. on old churches.

Modern sculptors sometimes have intended their work to weather and decay. Others have required that their work be maintained as newly created. However, the intentions have sometimes been based on a "romantic" apprehension of the effects of the course of time. The sculptor Henry Moore expressed his view in the 1960s that bronzes in open air with time and with the action of atmosphere will "naturally" turn to a beautiful green. He stated that "...sometimes [the artist] can not wait for nature to have its go at the bronze, and the process can be speeded up by treating the bronze with different acids which will produce different effects as black, green and red coloration..."[35]

Evidently, the generally altered appearance of copper roofs and bronze sculptures during the initial phase of the industrial epoch changed the apprehension of what was a desirable patina - moreover it changed the conception of what was assumed to be natural. What was commonly thought to be a result of natural causes was in fact the result of man-made atmospheric pollution. When the unpleasant side of industrialism was brought into fashion as a "natural" phenomenon the criticism vanished.

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[30] Mattsson and Holm, 1964. After a few years however the artificial patina on the City Hall was flaking. The copper roof was relaid again and artificially patinated in the 1940s with the same result as previously.

[31] Weil *et al.*, 1982.

[32] Hughes, 1992.

[33] Vernon, 1932.

[34] Mattsson and Holm, 1964; Mattsson and Holm, 1967. The Cathedral of Linköping and the St Clara Church in Stockholm were re-laid with this pre-patinated copper in the middle of the 1960s; and the Christine Church in Göteborg and the House of the Nobility in Stockholm were partly re-laid in the 1960s; from Aineli, 1997, unpubl.

[35] James, 1992.

However, Jack[36] was one important exception to the common approach, and in 1951 he published observations on the disastrous effects of the highly corrosive atmosphere in London, causing a less pleasing appearance of bronze statues. He gave close instructions for the maintenance and cleaning of bronze statues and stressed the importance of treatment during the early stages of exposure to weathering. According to Weil,[37] his work was largely ignored by both scientific and conservation communities. Not until the 1960s, one century after the investigations in Berlin, did consciousness about the effects of air pollution awaken in the world. The gilded bronze horses of St Mark's basilica in Venice attracted much attention, as they were understood to be threatened by the highly polluted environment.

2.3 The modern concern

The emergence of concern for open-air cultural material was perhaps rooted in the development of certain attitudes that became pronounced after the founding of IIC in 1950 and ICCROM in 1959. The first Director of ICCROM, Harold Plenderleith, recognized the necessity of looking at the world's cultural property as a whole. He articulated three basic assumptions: global embrace, no arbitrary boundary between outdoor and indoor cultural material, and obliteration of falsely constructed barriers between *preservation* and *direct conservation*.[38]

With this new attention on outdoor cultural material the way was open to dealing with outdoor metal sculpture. At the seventh session of the Committee for Scientific Museum Laboratories ICOM (International Council of Museums) meeting in Leningrad in 1963, a world-wide study of the problem of outdoor metal sculpture was initiated. John Gettens, who was a museum chemist specializing in the study of archaeological bronzes, was appointed for the task and reported on the subject in 1967. According to Weil, he was not aware of the German studies from the 1860s describing the effects of air pollution. Unlike Vernon, who ascribed only desirable qualities to copper corrosion products, he supported Jack to some extent in the fact that the change of outdoor metals might not always be desirable and that the atmospheric pollution played some role in these changes. However, Weil means that Gettens was not aware of the corrosion damage that had occurred on outdoor bronzes and the corrosion in progression. The extensive examinations and alarming condition of the Venice Horses were not mentioned in Gettens' report, but just referred to in the bibliography.[39]

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[36] Jack, 1951.

[37] Weil *et al.*, 1982.

[38] Weil, 1987.

[39] Weil, 1987.

Gettens' approach to bronze sculpture conservation was characterized by his archaeological perspectives and was probably influenced by the tradition of regarding patina as highly valuable. It is evident that different properties of an artefact may be evaluated differently by specialists from various fields. With the introduction of "scientific conservation" of museum objects the emphasis in treatment of archaeological objects also moved from the aesthetic aspects to using objects primarily as research documents. This attitude was influenced by the recent (1964) declaration of the Venice Charter[40] where the "monument" was regarded as an authentic message from the past and the documentary evidence was stressed. Patina was regarded as of documentary value of great importance, as a true imprint of culture and history. Hanna Jedrzejewska,[41] of the Research Laboratory at the National Museum in Warsaw, was concerned with ethics in conservation and supported this attitude towards archaeological objects. She claimed that artefacts should be considered as "documents of the past" and stressed the disadvantage of cleaning. In Gettens' conclusions and recommendations regarding outdoor bronze sculptures, he urged a focus on the compilation of case stories of practical methods by "someone with engineering training" to produce a monograph on the care and preservation of outdoor metal sculpture.[42] Weil[43] comments that he neglected the fact that conservation should be based on both scientific and humanistic considerations and be performed by skilled practitioners professionally educated in both sciences and humanities, bridging gaps between scientific requirements and technical studies and the demands of aesthetic and historic values.

The alarm sounded by the threat to the Venice Horses in 1965 was the major impetus for the modern concern.[44] As air pollution was targeted as the prime destructive source, and with the realization that such world treasures would have to be brought indoors, a major shift in attitude occurred. This change in attitude is comparable to the paradigm shifts, described by Kuhn,[45] when revolutionary scientific discoveries result in a major change in the perception and evaluation of familiar data, research methods and world-view. Thus, in the late 1970s, it had become well established that acidification is a rigorous problem of wide range. In the present case reasons for the change in attitude was also economic, such as the fear that tourism would suffer or maybe the realization that indoor sculpture might raise museum profits.

At the ICOM Conservation Committee meetings in Madrid in 1972, observations on serious corrosive attacks from air pollution were pointed out. Papers with descriptions of

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[40] Rosvall, 1988a; Jokilehto, 1988; Feilden, 1988.
[41] Jedrzejewska, 1961; Jedrzejewska, 1980.
[42] Weil, 1987.
[43] Weil, 1987.
[44] Weil, 1987.
[45] Kuhn, 1970.

technical analysis, new approaches to treatments and initiation of research of protective coatings, were presented by Riederer and by Lehmann.[46]

Interestingly, there were many successive observations of deterioration of bronze sculptures during the 1970s and several publications were written.[47] Increasing deterioration of facades of buildings were also reported during this decade.[48] This may signify that attention was drawn to the problems. Another cause may be that an actual change in the appearance of patina had suddenly occurred. Old photos of the equestrian statue by Saly from 1770 in Copenhagen show the change in the patina of the sculpture between the years 1912, 1962 and 1982, and reveal that the sculpture was mainly dark at the beginning of the century but has successively appeared lighter, especially during the last decades.[49] A sculpture of Rodin which was brought indoors in Copenhagen in the 1960s is still preserved in the state it displayed at that time. It exhibits mainly a dull opaque black patina with evidence of an initial development of light green patterns.[50] According to Gettens' previously mentioned investigation from the 1930s,[51] the patina on the examined 35-year-old sculpture was mainly dull black as well. Livingstone[52] also reported that the pattern of black and light green has been especially evident in the patina of the Statue of Liberty in New York since the 1960s, which may be interpreted as showing that the colour contrasts have increased.

It is obvious that the general appearance of sculptures has changed as a result of the changing environment. According to the above-mentioned observations, many sculptures during the first part of this century were covered with black corrosion crusts, evidently caused by the large amount of soot in many towns at that time. However, it seems that parts of the black matter have gradually been washed away by the rain during the last decades. Since the soot content and SO_2 concentrations have decreased in some parts of the world, the corrosion crust formed today may accordingly be expected to develop differently. At the same time other pollutants have increased, and the acidity and components in precipitation have changed causing other deterioration mechanisms to be dominant (see section 7). It may be noted that sculptures in some parts of the world, where the air pollution situation has developed differently and pollutant levels have just recently decreased, may exhibit appearances that resemble the sculptures described above in the first part of this century.

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[46] Riederer, 1972a; Lehmann, 1972.

[47] Weil, 1974; Riederer, 1972b; Weil, 1975; Kalish, 1975; Alunno-Rossetti and Marabelli, 1976; Riederer, 1977; Ogburn *et al.*, 1977; Kim, 1977; Gaspar *et al.*, 1978 Kalish, 1978; Nosek, 1978; Perocco, 1979; Alessandrini *et al.*, 1979.

[48] Rosvall, 1988a.

[49] Strandberg, 1986.

[50] Strandberg, 1986; "Borgarna från Calais" (1903), Glyptoteket, Copenhagen.

[51] Gettens, 1933.

[52] Livingston, 1991.

Weil,[53] an American art historian and conservator, was an enthusiastic pioneer in the field of conservation and started her work in the 1970s. She wrote vividly and with commitment about the problem. Her distinct claim was that the green patina was neither attractive nor protective. She criticised the narrow attitude implying that conservation treatments can be established solely on scientific facts and stressed the need of humanistic components of the activities, e.g. art-historical and aesthetic aspects. Her conviction was that the necessary development of the field would be acquired by a continual interplay between theory and practice and with a multiplicity of choices for conservation treatments. Weil further stated that the issues of value and significance should be integral parts of the treatment of cultural material and that the basic assumptions should be clearly formulated, examined and debated. She emphasized the need to consider each object as an individual case and to use treatments appropriate to its needs.

Since the early 1970s, activities in the field have dramatically increased and many scientific examinations have been performed on outdoor bronze sculptures in the 1980s and 1990s regarding alloy and patina composition.[54] Diverse approaches to conservation have been practised by different options of intervention and many methods of conservation treatment have been tested.[55]

Several important interdisciplinary meetings on outdoor sculpture have been held during the last decades. To mention some, three significant conferences were held in the United States in 1983 relating to conservation of outdoor monuments.[56] In 1986, ICCROM organized a symposium in Paris[57] on metal statuary and architectural decoration, and a conference regarding the Statue of Liberty restoration was held in New York.[58] In 1989 a comprehensive symposium was arranged by NACE[59] (National Association of Corrosion Engineers) in Houston, Texas, for conservators, curators, environmental scientists, and corrosion engineers.

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[53] Weil, 1984; Weil, 1987.

[54] Scientific examinations of sculptures: see **Paper II**; Holm, 1981; Fiorentino *et al.*, 1982; Weil *et al.*, 1982; Lins, 1983; Forshell, 1984; Angelucci, 1987; Burmester and Koller, 1987; Franey and Davis, 1987; Nassau *et al.*, 1987a; Opila, 1987; Mach *et al.*, 1988; Marabelli, 1992; Mach and Snethlage, 1989; Reger, 1992; Block *et al.*, 1990; Timofeeva *et al.*, 1990; Dolske and Meakin, 1991; Robbiola and Hurtel, 1991; Ammannati *et al.*, 1992; Meakin *et al.*, 1992; Robbiola *et al.*, 1993; Vendl *et al.*, 1994; Pichler *et al.*, 1994; Gullman and Törnblom, 1994; Selwyn *et al.*, 1996.

[55] Conservation of outdoor sculptures: see Socha *et al.*, 1980; Weil, 1980; Fiorentino *et al.*, 1982; Weil *et al.*, 1982; Riederer, 1982; Naudé, 1983b; Tatti, 1983; Riss, 1983; Weil, 1983; Zelst and Lachevre, 1983; Angelucci, 1987; Marabelli, 1987; Weil, 1987; Hawkins, 1987; Pardue, 1987; Roidl, 1987; Johnson and Püringer, 1987/88; Beale, 1992; Cass, 1992; Lins, 1992; Panhorst, 1992; Forshell, 1990; Herrmann, 1990; Herrmann, 1990; Burrini, 1992; Merk-Gould *et al.*, 1993; Römich, 1993; Gullman and Törnblom, 1994; Harris, 1994.

[56] Beale, 1992. The conference "Sculptural monuments in an outdoor environment" resulted in a publication: see Naudé, 1983c.

[57] ICCROM, 1987.

[58] Baboian *et al.*, 1990.

[59] Drayman-Weisser, 1992.

In Europe the Eurocare-Copal project (EU 316)[60] was initiated in 1987, aiming at investigating the atmospheric corrosion of several copper alloys in diverse environments, the final aim being to develop conservation treatments for bronze monuments. Activities are carried out in different countries within this field, and meetings are held yearly for the members.

At the present time in the 1990s, one of the major issues regarding outdoor bronze sculpture conservation seems to be connected with the complex character of the problem and with the difficulty of formulating an unambiguous approach. The changing appearance that is due to the corrosion process may in some cases be regarded as desirable and sometimes not. Conservation treatments are often controversial since there are conflicting views in ethics and aesthetics. Since outdoor sculptures are part of public art, conservation interventions also may cause strong and diverse reactions among people due to the various values that are assigned to the objects (see section 2.4.1). Such conflicts in some cases lead to bewilderment and may result in the easiest approach to conservation, thus disregarding the problem altogether.

Regarding copper roofs, the main concern nowadays seems to be the impatient waiting for copper to turn green. This expectation is not always fulfilled fast enough in cases where objects are located remote from towns, in places where pollutant levels are low. As an example, it might be mentioned that Lysekil church, situated in a small town on the west coast of Sweden, was roofed with new copper sheets in the beginning of the 1970s.[61] The roof has turned darker brown but only achieved a slight white greenish hue after about 25 years of outdoor exposure. In contrast, some big buildings in Göteborg city which were roofed with new copper sheets in the 1980-90s[62] have already turned greenish after much shorter exposure in a more polluted environment. The patented method for green patination of copper roofs, described above from the 1960s, has recently again come into industrial production at Outokumpu Copper AB, and has been applied on some big buildings.[63]

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[60] See e.g. Eurocare-Copal report, 1994.

[61] Hedling, 1997, unpubl.

[62] Hedling, 1997, unpubl. Buildings roofed with copper sheets during the last decades in Göteborg were Hotel Sheraton, early 1990s; the City Theater building, 1980s; the Stockhouse, ~1985; the Concert hall, ~1983.

[63] Aineli, 1997, unpubl. The roofs of Helsinki Cathedral, Finland, 1996; and Linköping Museum, 1995; were relaid and patinated with this method, named "Nordic Green". Moreover the roof of the new building for the British Opera in Covent Garden in London will soon be patinated.

2.4 Modern theory

According to Fielden,[64] cultural property brings a vital message from the past that promotes the understanding of ourselves and from where we came. These resources communicate messages from various cultures and help to improve the quality of life. He states that cultural property belongs to all, as individuals as well as on the level of society.

Conservation has been defined as *"the dynamic management of change to reduce the rate of decay"*.[65] This concept may also be expanded to the wider meaning that conservation is a fundamental way of thinking, a paradigm that can be applied to several types of domains.[66] Thus, conservation may be defined as *"a problem-oriented activity devoted to preserving natural, cultural and social resources in a process of change"*.[67] Other paradigms may imply that conservation is not important, or that it is not a problem at all. According to Kuhn[68] the paradigm is a filter anywhere in science and practical work, and it is our responsibility to be aware of the effects scientific results have in practice.

Conservation is a holistic discipline which offers an integrated, well-defined cross-disciplinary competence. It implies a combined understanding of the material and the intangible and anthropogenic conditions of cultural heritage.[69] The various perspectives should be integrated and balanced to meet as many requirements as possible.

When studying the problems of bronze sculpture conservation, the theory of system design may be applied. van Gigch has conceptualized a hierarchy of systems which have different levels of abstraction and of logic.[70] The basic levels in this hierarchy are:[71]

– *The metamodelling level* is the highest level of abstraction and is extremely necessary in such a complex multidisciplinary field as conservation. At this level evaluative standards are determined from the prevailing system of values. The foundations of the process are decided at this level.

– *The modelling level* is where the problems are studied in a scholarly-scientific way. It may involve analyses and explanations of deterioration as well as of interventions of conservation. Specifications and requirements of all kinds of interventions are formulated at this level.

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[64] Feilden, 1991.
[65] Feilden, 1979.
[66] van Gigch, 1992.
[67] Rosvall *et al.*, 1995.
[68] Kuhn, 1970.
[69] Rosvall *et al.*, 1995.
[70] van Gigch, 1991.
[71] Lagerqvist and Rosvall, 1995; van Gigch *et al.*, 1996.

– *The intervention level* means the operative level. At this level, activities are carried out, e.g. as direct conservation treatment.

This hierarchy of inquiring systems is a deliberate thinking process which enables the understanding of problems through a process of abstraction. The approach is further outlined and applied to bronze sculpture conservation below.

2.4.1 Values

Conservation is driven by motivations and values which reside in the metalevel system. The question of why we conserve is grounded in values and beliefs.[72] The issue of value and significance is an integral part of the treatment of cultural material. As France-Lanord stated in 1976 "it is because of [the message of an object] that man is anxious to conserve the object, not because of its matter".[73]

The questions of value and significance are outlined by Riegl and Feilden.[74] According to Feilden, a hierarchy of values in order of priority and their criteria should be taken into account, to preserve and to respect the essential message of the object. The description below is based on Feilden's classification of values in three main categories and different sub-values. However, the model here is modified for values relevant to bronze sculptures and the criteria are further outlined. The system is presented only for identifying the values and not for valorization. Cornell[75] describes the double reality of architecture, being an aesthetic organisation of practical reality. Outdoor public sculptures may analogously be regarded as possessing this double nature, mainly being conceived as works of art but even having meanings in practical reality.

Emotional values are those which can be felt without necessarily being able to articulate them clearly in a verbalized mode. According to van Gigch *et al.*[76] these are the values that allow us to affix desires to certain things, concerning intangible existential dimensions, often of collective concern.

–*Wonder* embraces all the questions that arise when confronted with an artefact – a wonder at the miracle of artistic creation.

– *Identity* is the sense of belonging. Cultural heritage may contribute to the feeling of self-identification and may combat alienation in a rapidly changing society.

– *Continuity* reminds us of links between the contemporary generation and the historical past, and reassures us about permanence when facing the future. Conservation

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[72] van Gigch, 1992.

[73] Weil, 1987.

[74] Riegl, 1982; Feilden, 1988; Feilden, 1991.

[75] Cornell, 1968.

[76] van Gigch *et al.*, 1996.

measures causing sudden evident changes in the appearance of a sculpture sometimes arouse strong reactions among the public audience. The alterations caused by the corrosive species in the atmosphere, however, are generally slow enough for the general population to become used to the change and have often been easily accepted without recollection of the original appearance.

– *Veneration* may be held for religious places and relics, the person erected on the pedestal or, in the cult of artists, the sculptor who created the work of art. Veneration is occasionally discernible behind stylistic revivals and other strong restoration interventions.

– *Symbolic values.* Statues are symbols sending messages of e.g. power, honour, liberty, and beauty. The perception of the symbolic information depends on cultural and emotional awareness. Monuments have been erected to symbolize the achievements of great men, their power and strength, and an aged patina in this context may send a message of past time and past values. Also in modern sculpture the symbolic value is often an essential message of the object.

– *Spiritual values.* Cultural heritage may provide spiritual dimensions, e.g. when entering an ancient temple, church or building, or when contemplating a work of art.

Cultural values

– *Documentary values* are formed by historical evidence provided by an artefact. If these qualities are destroyed the monument may be reinterpreted.

– *Archaeological values* of a monument involve its unexplored potential and depend on maximum retention of the original material. This includes the fact that ageing may be a quality in itself. The monument's patina is the visible sign of ageing and it contains information on the passage of time. It is a testimony which carries the message of decay at the current time. Riegl[77] defined these values as *age-values* at the turn of the century. It seems that he had a nostalgic appreciation of decay and discovered the degradation of culture to be of value to culture itself.[78] Age-values are considered to embrace all artefacts, without regard to their original significance and purpose, as long as considerable time has passed.[79]

– *Newness-values*, according to Riegl[80], are rooted in the priority of youth over age. New and whole things are considered to have values that may be obtained by e.g. restoration to their appearance as if newly created. These values can be preserved only at the expense of age-values.

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[77] Riegl, 1982.

[78] Forster, 1982.

[79] Riegl, 1982.

[80] Riegl, 1982.

– *Art-historical values* may deal with the artists' lives and intentions. According to Riegl,[81] these values might be preserved by maintaining objects as genuine as possible, as documents for future art-historical research. Symptoms of decay, being the essence of age-values, in such cases have to be removed. It is common that these kinds of values are emphasized, referred to as the artists' intentions, in outdoor bronze sculpture conservation today. This approach legitimatizes restoration interventions which in many cases have a stylistic character.

– *Technological and scientific values* can tell about the civilization in which a sculpture was created. Monuments carry technological and technical information about the making and working of the material, as well as information about the craft and production, e.g. of casting and surface tooling. Tool marks can be found in the "original surface" of an object. This signifies a level in the patina showing the original morphology of the surface. The "original surface" is not necessarily coincident with the original surface level, but can be a pseudomorph.

– *Artistic values* and *aesthetic values* are closely related and are often confused. In connection with works of art the concept *artistic values* is commonly used and is assigned to properties in aesthetic organisations produced by artists. The artistic properties of a sculpture reside in conceptual, morphological and coloristic characteristics. The appropriation and appreciation of these characteristics is in many respects subjective and contemporary, and may change from generation to generation. Riegl[82] was first to clarify in a scholarly model the subjective character of these values, and defined them as *art-values*. Feilden uses the term *aesthetic values* when referring to all kinds of cultural property. This concept is wider than the first mentioned and includes many subjective and emotional aspects. An aesthetic experience is an overall experience which is partly related to the beholder. Everything may be aesthetically experienced, e.g. nature, music, objects and not just works of visual art. The aesthetic values are independent of the artists' intentions and some works of art even lack such characteristics.[83]

– *Townscape and landscape values*. Sculptures may be designed for their specific location. Alterations in the surrounding environment can negatively affect the message of the object.

– *Gender values* are suggested to be included as they are profoundly reflected and demonstrated in sculptures. The majority of large monuments are erected men, made by men and commissioned by men. They were in previous periods located in towns planned by men for men, but are today perceived by and available for both men and women. Men's dominance and control in public spaces is thus still prevalent.

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[81] Riegl, 1982.

[82] Riegl, 1982.

[83] Brunius, 1986.

Use values

– *Functional values* are not necessarily favourable to the preservation of the cultural values. Water fountains, sculptural parts frequently touched by man, and sculptures inviting and intended for children's climbing, are examples of objects having a practical function that may be a threat to the material properties and intrinsic symbolic values of works of art. On the other hand, traces of such practical use can be of importance for the true interpretation of the image of the sculpture. The sculptor Henry Moore first appreciated children climbing on and people touching his works of art, but later in life changed his opinion on this issue due to marked wear of some of his sculptures.[84]

– *Economic values* may be related to artistic and aesthetic dimensions and scarcity of the object. Tourism and education are other aspects which can be connected with economic values.

– *Social values* may be assigned to objects illustrating social history, indicating how past generations have lived and thought. These values give a sense of identity and continuity to citizens. Prestige of owning a work of art is also related to social values.

– *Political values* can be used to establish the history of a nation in people's minds. This is quite important for relatively new nations and communities, and accounts for many big projects. Great publicity can be gained by large restoration programmes and is economically supported, while minor acts of preventive maintenance may not win the same attention. The message of a monument can also be revived and be brought to life by a restoration project. The restoration of a symbol of power may confirm intangible power, since the foundations of power are supported by material structures. The preservation of the actual state or the decay may favour other messages.

The values are to be used as instruments for analysing qualitative properties of cultural resources. The intangible characteristics, messages, etc. that become prominent, as well as the material properties of the objects that are favoured by decay, conservation or restoration, should be considered on an individual basis for each single object. The question of whose values are represented and for what reasons may also be relevant. Should it be those of specialists, of trustees, of politicians, of local public opinions, of visiting tourists, of men, of women, of the older or younger? If cultural property belongs to the general public audience, individuals as well as distinct social groups, and is essential to civilization and quality of life, the collective responsibility should be stressed. The recent Nara document,[85] accordingly, emphasizes respect for all cultures in the judgement of values.

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[84] Sommers, 1995, unpubl.

[85] Lemaire and Stovel, 1995, p. xxi.

2.4.2 Scholarly-scientific research in conservation

At the modelling level of conservation, problems are studied in a scientific way, as a discipline of its own. "Normal science" in basic disciplines, e.g. chemistry and art history, as well as cross-disciplinary work and competence are at the same time important for the field.[86] Besides natural deterioration, a large number of man-made factors influences the process of deterioration in the industrial society. The understanding of these processes and, based on this foundation, how materials and various structures should be treated using relevant measures contain a multitude of unanswered questions.

The dominating positivistic tradition of modern science is intrinsically characterized by reductionism. It has been very successful in decomposing the world of nature into the fragments of its whole. However, reductionism is not sufficient to explain and to understand complex phenomena, and the fragments and the whole are necessarily to be linked by analytical and synthetic thinking. Methodological reduction, i.e. analytical thinking, is important to understand the structure of various systems in relation to their elements, but a holistic view, i.e. synthetic thinking, is necessary to understand the interactions and relations between the systems.[87]

This dissertation primarily deals with the modelling level, asking questions concerning deterioration processes on copper and bronze. Methodological reductionism is applied to seek explanations, by investigating the underlying corrosion mechanisms at lower levels of complexity. Laboratory exposures are used to find crucial deterioration mechanisms in the atmospheric corrosion. In this way the existing body of knowledge may be extended, with implications on all levels ranging from intervention, based on modelling to the metamodelling level, to be able to predict future needs for the performance of interventions.

2.4.3 Interventions by conservation

The prevailing values may be revealed in the method of intervention chosen for a specific object. It is important to be aware of the values underlying decisions, not to be manipulated by and act after paradigms which are not supported. Practical problems such as economy, however, restrict many kinds of actions.

Matero[88] underlines the important fact that decisions concerning selection of conservation treatment often take place without a professional conservator involved in planning and/or execution of conservation interventions. Professional conservation practice presumes an understanding of the intent of the artist, considerations of the users,

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[86] Rosvall *et al.*, 1995; Rosvall, 1988b.

[87] Wuketits, 1987.

[88] Matero, 1993.

and the effects of time and its implications for the object. Moreover, the practice assumes a knowledge of treatments according to the principles established.

Practice of conservation must take into account values which people attach to objects when interventions are applied.[89] If it is decided that decay has to be reduced, interventions may be exercised in different ways to preserve qualities of significance. According to Feilden[90] all interventions should be minimized as they always involve some loss of value, besides other implications. Different degrees of intervention are identified which can take place separately or simultaneously in conservation treatment.

– *Prevention* of deterioration may include planned measures after diagnosis, e.g. to reduce atmospheric pollution. Preventive measures for new sculptures may be the consideration of appropriate patination methods for sculptures and locations for inauguration, as well as regular professional inspection and maintenance plans to prevent the development of undesirable changes.

– *Preservation* signifies the effort to keep cultural property in the existing state, e.g. by maintenance, including superficial cleaning of surface dirt and repair. By removing corrosive agents such actions may preserve sculptures from deterioration.

– *Consolidation* is the addition of supportive materials to ensure structural integrity. This includes application of coatings to preserve patina of sculpture from corrosive atmosphere and acid rain, e.g. by waxes, acrylic lacquers or silicon-based products. Preservation by consolidation may be executed with the aim to "freeze" objects in the existing state with use of conservation materials regarded as "reversible", and sometimes with material that is supposed to be long-time durable. A new concept, "retreatability", was introduced by Appelbaum[91] and refers to the use of material and intervention methods which allow future treatment.

– *Restoration* is the renewal of material components, which implies the revival of an original concept or legibility of an object, e.g. in cases where random coloration of corrosion and crusts visually destroys sculptural form and reading of surface texture. This may include total or partial removal of corrosion products, mechanically (e.g. by metallic wool; abrasive pads; abrasive tools; peening with sand, glass beads or granulates of walnut shells; or by ultra-high-pressure water) or chemically (e.g. by complexing agents or acids). After removal of corrosion products, repatination of the sculpture may be performed with chemicals. Restoration is often a controversial issue. The main motives for such actions often are based on aesthetic and/or functional considerations, and not primarily on efforts to reduce the rate of decay.

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[89] van Gigch *et al.*, 1996.

[90] Feilden, 1979; Feilden, 1988; Feilden, 1991.

[91] Appelbaum, 1987.

– *Reproduction* implies copying an extant artefact, e.g. when the original version has to be moved. Such protection of an authentic work may be the case for sculptures of exceptional value, or when an object is threatened by the surrounding environment.

– *Reconstruction* must be based on accurate documentation. A missing part of a sculpture may be reconstructed since it sometimes is necessary in order to re-establish visual appearance and meaning. However, it should neither replace nor compete with the original work or with the conservation process, but be an integral part of the object.

2.4.4 Ethics

A code of ethics dictates the accepted rules or standards for legitimate professional conduct and proper layman behaviour. Standards of conservation have been developed to guide intervention for all kinds of cultural property and are found in some of the recent documents[92] including: the AIC document (revised 1979), the Venice Charter (1964; revised 1978), the Burra Charter (Australia ICOMOS 1988), and the Nara document (1995). All these documents identify the conservation process as one governed by absolute respect for the aesthetic, historic, and physical integrity of the object with a high sense of moral responsibility. This implies obligations that fall into the following categories according to Matero:[93]

– *to perform research and documentation,*
i.e. to record physical, archival, and other evidence before and after any intervention;
– *to respect cumulative age-value,*
i.e. to acknowledge the work as a cumulative physical record of human activity embodying cultural values, materials, and techniques;
– *to safeguard authenticity,*
i.e. according to the recent Nara document on authenticity,[94] to respect and understand the values attributed to the heritage. The document stresses that it is not possible to base judgements of value and authenticity on absolute criteria, since judgements about values may differ from culture to culture, and even within the same culture;
– *to perform minimum reintegration,*
i.e. to re-establish structural, aesthetic, and semiotic legibility with the least possible interference with the original;
– *to perform interventions* that will allow other options and further treatment in the future. This principle has been based on "reversibility" as the major criterion but has been redefined more accurately by Appelbaum as "retreatability".[95] The latter concept is of

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[92] Naudé, 1983a; UNESCO, 1978; ICOMOS, 1988; Lemaire and Stovel, 1995.
[93] Matero, 1993.
[94] Larsen, 1995.
[95] Appelbaum, 1987.

considerable significance for architecture and outdoor monuments in corrosive environments.

2.5 Conservation in different parts of the world

This presentation is not intended to give a complete overview of different types of conservation measures executed throughout the world, but should only be regarded as a selection of some prominent methods, performances and pronounced attitudes within bronze sculpture conservation. Much more conservation work has been carried out in different countries than is described in this section, which is based on publications primarily in English and some personal communication. The section has nevertheless become extensive and has been difficult to confine to an appropriate part of this dissertation. The review is considered to contribute to the comprehension of the development during the last decades, the general tendencies of importance for a global understanding and various conservation measures depending thereupon.

Outdoor bronze sculpture conservation, to a significant extent, has only been performed during a few decades, and much more research and practical experience are still needed within this field to cope with existing problems. Different attitudes of professional categories involved in decisions and measures have reflected the approaches chosen when tackling the problems and the means of communicating. Discourses are formed by different traditions in scholarly disciplines, in craftsmanship, and even within the discipline of conservation.

It should be stressed that the below-described mistakes, debates, professional criticism, and strong public reactions experienced in the interventions performed, may have been necessary for the development of the field, contributing to the comprehension and elucidating the innumerable aspects of the problems. Future work should make use of this history and of the accumulated knowledge of these experiences to avoid the repetition of severe mistakes. A general tendency within bronze sculpture conservation seems to be towards preventive conservation, maintenance plans, and minimal and retreatable intervention performances, abandoning strong intervention measures such as stylistic restoration.

2.5.1 Europe

Sweden

In general, the care for bronze sculptures in Sweden is highly neglected, as is the case in many parts of the world. There are obviously no distinct plans for preservation of the public art existing on national or local levels. The responsibility for maintenance is spread among several trustees. Cleaning of sculptures, and other measures, are usually performed by non-professionals and are generally not documented. E.g. some outdoor sculptures are regularly cleaned by high-pressure water, and sometimes alkaline washing detergents have been used.[96] Probably, several dubious methods have also been used around Sweden as well as in other countries, e.g. with acids, strong alkalis, and cleaning solutions aimed at the treatment of stone exteriors.

In a cross-disciplinary project at the end of the 1980s, regarding the effects of air pollution on buildings and monuments in Göteborg, two old bronze monuments were included and an inventory and damage analysis was performed.[97]

In Stockholm, some impulsive measures to protect bronze sculptures were carried out also at the end of the 1980s.[98] The use of methods developed for stone was advocated to protect bronzes. Patina compounds were removed, and the surface was fixed with chemicals and consolidated with a silane compound not previously tested. No aesthetic or ethical considerations were made before the rapid execution of the measures. A number of sculptures were treated before authorities and the public reacted, causing a lively debate in the daily press.[99] Loud voices demanded the immediate cessation of this performance. The treatment had caused the light green patina to change in some cases appearing as "cast iron", and expressions such as "pure vandalism" were used in the press. Moreover, the method has later proved to be irreversible since the surface coating is impossible to dissolve.[100]

The Conservation Institute of the Central Board of National Antiquities (RIK) was from 1989 engaged in research aimed at identifying the causes and extent of damage to the Swedish heritage. A bronze sculpture project concerned with examining damaged objects and their care and maintenance was included. A small part of this project was an in-depth study of 14 sculptures in Göteborg aiming at describing and characterizing various appearances on outdoor sculptures.[101] More work was performed by RIK in Stockholm, including examination and restoration of bronze sculptures. In the final report from RIK,[102] it was concluded that most of the outdoor bronzes in Sweden, whatever they looked like, were not seriously damaged. The approach was that outdoor corrosion of bronzes was a rather harmless process since pitting depth in the metal was regarded as being relatively low (less than 0.5 mm in a hundred years). The implication of this was that sculptures less than 50 years of age were not regarded as exhibiting any corrosion

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[96] Hellberg, 1993, unpubl.
[97] Börjesson *et al.*, 1990.
[98] Pühringer, 1990.
[99] See e.g. Lindström, 1989.
[100] Gullman and Törnblom, 1994, pp. 167-181.
[101] **Paper II**; Strandberg and Rosvall, 1994.
[102] Gullman and Törnblom, 1994, pp. 41-44, 52-54 and 68-70.

damage, which in this context was defined as metal loss. It may be noted, however, that even pits with a depth of a few µm normally result in a clearly visible etched pattern on the metal surface. The Swedish sculptures were not considered by the research team to be in need of extensive restoration. Some sculptures located in Stockholm, nevertheless, were regarded as in acute need of care and were restored. The conservation plan mainly aimed at achieving the artists' intentions using traditional methods of repatination. The restoration operations were executed by craftsmen (art founders and patinators) and included e.g. total removal of corrosion products using sand-blasting, repatination and waxing. Even this kind of restoration suffered some criticism in the press. Many sculptures in Stockholm, Göteborg and Sundsvall were inspected and were considered to be in a state of neglect. It was emphasized that outdoor works of art require regular attention and curative treatment in the form of washing and waxing.

Since 1988, the Swedish Corrosion Institute performs field exposures of patinated and surface-treated copper and bronze in different environments with the aim to promote preservation of outdoor sculptures.[103]

Denmark

In Denmark, the care of outdoor bronze sculptures has been focused on objects with structural damage. Broken parts have been mended by welding, and the part of the surface that has been repaired has been chased and patinated with chemicals. There is no systematic maintenance plan for outdoor bronze sculptures.[104] The general attitude prevailing in Copenhagen seems to be an appreciation of the relatively fast greening of sculptures occurring in the marine climate.[105]

Norway

Some sculptures from the 1940s in the Vigeland Park in Oslo have been treated regularly during the last years.[106] Bird-droppings, causing corrosion, were mainly cleaned off with water and brush, and a coating of beeswax was applied. The wax reduced the contrasts between dark and light green areas and integrated the legibility of the sculptural form. Some sculptures appeared somewhat darker and more glossy after the wax application. An interesting discussion arose in the daily press due to diverse opinions about this treatment.[107] The main arguments were not supported by facts concerning preservation, but the underlying reasons for some strong reactions were related to different attitudes to the greening and decay of the sculptures. Among several aspects that were brought up in this debate, one interesting dimension reflected the various feelings

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[103] Johansson, 1995.
[104] Malfilatre, 1997, unpubl.
[105] See e.g. Holm, 1981.
[106] Refsum, 1996.
[107] In daily press, sommer 1996. See e.g. Refsum, 1997.

for Vigeland's works of art and the diverse appreciation of their artistic values. Thus, greening was advocated in cases when some negative feelings for the sculptures were discernible, and on the contrary increased legibility of the artistic expression through wax treatment was supported when more positive feelings for Vigeland's art dominated.

Finland

In Helsinki the Finnish Sculpture Association has played an active role in trying to collect information about causes of decay and to establish conservation principles of bronze sculptures. A working party for bronze sculptures was founded in 1990, consisting of artists, art historians, conservators, founders, corrosion scientists and administrators. A training programme for various professionals working with outdoor sculpture maintenance was developed. The care for new sculptures was stressed, and all sculptures were recommended to be washed twice a year by water and brush. Recent interest has been focused on the maintenance of the sculptures in the city, since Helsinki has been selected as "Cultural Capital of Europe" in the year 2000.[108]

United Kingdom

Since the 1950s, more than 100 outdoor bronzes owned by the City of London have been treated regularly. Corrosion products and accretions have been removed after which a coating of lanolin, beeswax or paraffin has been applied, sometimes in a mixture. Dark pigments have also been added to the coating. The regular removal and replacement of many of the London bronzes is still executed, four times a year.[109] This tradition results in a shiny black opaque "licorice-man"-like appearance of sculptures, which in colour and opacity to some extent resembles the black dull surface caused by soot. Since this kind of treatment has been performed regularly since the 1950s, these sculptures do not appear green as is most well-known nowadays. Seemingly, there has not been any heavy criticism against this kind of treatment, probably since the London citizens since long ago are used to the blackish appearance of sculptures caused by the heavily polluted air during the industrial epoch.

Harris,[110] however, a freelance conservator in the UK, claims that most public sculptures in the UK are neglected, and that the conservation efforts that are made fall into the category of refurbishment using techniques which can cause extensive damage, or fail on grounds of aesthetics. Harris has treated some of the monuments in London during recent years using partial removal of corrosion by mechanical cleaning, partial patination with sulfides to integrate the colour contrasts, and surface treatment with so-called Renaissance wax (wax paste based on micro-wax).[111]

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[108] Wikström, 1994; Wikström and Kanerva, 1997, unpubl.

[109] Weil, 1980.

[110] Harris, 1994.

[111] Harris, 1995, unpubl.

At the Henry Moore Institute in Perry Green outside London, the approach to conservation is devoted to the sculptor Henry Moore's view. The artist believed strongly in the effect of "nature" on his works (see section 2.2). Weathering of the bronzes may therefore continue, but if undesirable changes occur interventions are performed, e.g. with chemicals, to "help nature" and provide for the artist's intentions. The general conservation policy is maintenance by regular cleaning and waxing. Conservation is performed by his former assistants, who worked with the sculptor in his lifetime and are supposed to have a sound knowledge of the artist's attitudes.[112]

Germany

Riederer has reported extensively on the care of outdoor monuments in Germany, and he has performed many investigations since 1970 on the conservation of monuments in Munich and Berlin.[113] He recommends the removal of corrosion products (by sand-blasting, grinding and polishing) for older sculptures, and surface protection with lacquer and waxing.[114]

In Bavaria[115] the conservation of bronze monuments is reported to be limited to the controlled mechanical removal of disfiguring black crusts and lime deposits by scalpels and rotating brushes. The bronzes are then washed with water and brush. Microcrystalline wax is applied, thus integrating the appearance and giving the surface some lustre. The conservation treatment is inspected at least every two years and is then partly improved.

A new type of coating, an organic-inorganic copolymer called Ormocer, has been designed by the Fraunhofer-Institut für Silicatforschung, to protect outdoor bronze sculptures. It has not yet found any large use on the market.[116]

Italy

In the early 1960s, with the recognition of the threat to the Venice Horses of San Marco, an interest in the problem awakened in Italy as well as in other parts of the world.[117] Many important monuments have been treated in Italy since that time,[118] including the gilded Horses in Venice, the Lion and Griffin of Perugia, the Fountain of the Turtles, the Florence Baptistery doors, and Verrocchio's Christ and St. Thomas. In the National Italian Conservation Institute (Istituto Centrale del Restauro),[119] the reported standard

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[112] Sommers, 1995; Sommers, 1995, unpubl. See section 2.2 about Henry Moore's intentions.

[113] Riederer, 1972b.

[114] Riederer, 1982.

[115] Brendel *et al.*, 1994.

[116] Römich, 1993.

[117] Weil *et al.*, 1982.

[118] Alunno-Rossetti and Marabelli, 1976; Perocco, 1979; Alessandrini *et al.*, 1979; Weil, 1980; Fiorentino *et al.*, 1982; Angelucci, 1987; Dolcini, 1992.

[119] Marabelli, 1987.

intervention procedures for outdoor bronzes were mechanical or chemical cleaning of particulate deposits, stains and encrustments, the final treatment being a protective surface coating. Use of multiple-layer protective coatings, including natural and synthetic waxes applied over acrylic coatings, as well as other synthetic polymers have been investigated.[120]

France

Regarding bronze sculptures in France, measures performed are a blend of traditional restoration by bronze-casting companies using methods of complete removal of corrosion products and repatination, and a new conservation approach including soft mechanical cleaning with walnut shells or other vegetal abrasives, and microcrystalline wax treatment. Maintenance plans are just occasionally established nowadays, but a promising trend indicates preparation of such programs.[121]

Poland

In Warsaw work was carried out on the sculpture of the Polish king Sigismond III Waza, which implied a complete restoration and a repatination with a thick new oxide coating.[122]

Russia

Several monuments in St Petersburg and Moscow are protected by wooden shelters from the high atmospheric precipitation in the autumn-winter season. Investigations concerning the use of protective barriers of polymers are also performed.[123]

2.5.2 *North America and Australia*

USA

In the USA many activities have been carried out in the field of bronze sculpture conservation during the last decades. Between 1972 and 1984 about 300 outdoor metal sculptures were treated, while previously treatments were rare.[124] Several conferences related to outdoor bronze sculptures have been organized in the USA.[125]

All established types of interventions have been implemented in the USA, from the restoration of sculptures to minimum intervention measures. Weil proposed total repatination as an acceptable course of action on certain sculptures in the 1970s and

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[120] Marabelli and Napolitano, 1990; Dolcini, 1994.

[121] Pennec, 1997, unpubl.

[122] Socha *et al.*, 1980.

[123] Sisov, 1994.

[124] Weil, 1987.

[125] See Naudé, 1983c; Baboian *et al.*, 1990, Drayman-Weisser, 1992.

1980s. In most work, total removal of corrosion products using peening with glass beads was exercised. Glossy acrylic coatings (Incralac) were applied after cleaning, thus intended to act as an inert protective coating.[126] However, time has testified to the extreme difficulty in removal of old lacquer, implying that this may not be considered as a reversible treatment.[127] As a consequence, the method later has suffered heavy criticism after the pioneering performances within the field. Tatti advocated a preservation approach, only removing surface dirt on sculptures, and proposed hot-wax treatment. Chase and Veloz recommended cleaning with soft abrasive, e.g. walnut shells, only to remove some corrosion in the patina layer. This cleaning was followed by application of a wax coating over the remaining corrosion products. One more "artistic" approach, performed by some conservators, involves partial repatination with chemicals to blend with existing corrosion.[128]

A major national initiative called Save Our Sculpture (SOS!) began in 1989, which reports on the contemporary condition of outdoor sculptures. Volunteers trained by conservators, scholars and individuals, implemented the survey using a questionnaire to report condition assessments. SOS! aims to raise public awareness about America's sculptural heritage and to promote responsibly on-going care for the works. From this basis a national strategy for preservation is planned to be developed.[129]

Canada

There is no standard treatment of bronze statues in Canada and the way it is performed in each individual case depends on the conservator. In Ottawa 16 outdoor monuments have been conserved in recent years by minimal intervention. This included thoroughly washing with water and detergent, partial patination of disfiguring streaks with diluted ammonium sulfide solution, and application of microcrystalline and polyethylene wax mixture, or in a few cases an Incra lacquer coating. A maintenance schedule has been established for these sculptures, with planned inspection performed once or twice a year.[130]

Australia

The National Capital Planning Authority, which commissions major public art-works in Canberra, is in the process of incorporating preventive strategies for new art-works.[131] Guidelines for designers of public art have been prepared with basic information on materials suitable for permanent outdoor art-works, to avoid safety, structural and

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[126] Weil *et al.*, 1982; Beale, 1983; Harris, 1994.
[127] Riss, 1983.
[128] Harris, 1994.
[129] Reger, 1992; Beale, 1992.
[130] Selwyn *et al.*, 1996; Selwyn, 1997, unpubl.
[131] Hughes, 1996.

aesthetic problems in the future. The author claims that the conservator has an ethical responsibility to do as much as possible to prevent problems, and that conservation considerations should be made before construction begins. She recommends conservators to be represented in organisations responsible for commissioning of public art-works. Conservators should also hold lectures in art schools about the nature of materials, and educate other professionals involved in outdoor public art as well.

2.6 Concluding discussion on conservation views for outdoor sculptures

Diverse approaches to conservation which could be named "conservation" and "restoration" approaches have occurred in parallel since the 19th century and have been debated during this time. On the one side *historic, scientific, documentary and age-values* of cultural objects have been emphasized, and on the other side *aesthetic, artistic and art-historical values* have been predominant.

Before the *industrial revolution*, outdoor copper and bronze, located in rural unpolluted inland areas, probably remained lustrous or dark brown for a long time. However, monuments of bronze have always tended to be located where human activity has been intensive and where some kind of air pollution consequently has occurred, causing green patina to appear in time. *Archaeological activities* during the 19th century, involving the evaluation of aged buried bronzes, probably affected the *appreciation of patina* on outdoor bronze sculptures.

During the early period of the *industrialized epoch*, strong reactions were expressed when monuments became *dull black* due to the increased burning of coal. Washing of monuments was performed to some extent to keep the sculptures lustrous. The criticism later vanished during industrial development, and the *light green patina* – which also was caused by the increasing air pollution – became much admired. The pollution-induced green patina was accepted as a *"natural"* phenomenon and became a new *aesthetic ideal.* In the modern conservation theory developed during the 1930s the general tendency was to avoid restoration and favour conservation, and a *scientific approach* began to form. Artificial patination by chemicals was used to obtain the green "natural" appearance on sculptures, and methods for the production of green artificial patina for copper roofs were developed even with the use of modern products. During the 1950s, the scientific conservation approach characterized the Venice Charter from 1964 where the monument was considered to remain as a message from the past and its documentary value was stressed.

In the 1970s, attention was beginning to be focused on air pollution as a prime destructive source. Many observations of deterioration of bronze sculptures were recorded, partly as a result of the increased *awareness of the problem* but probably also because an *actual change* of the sculptures became especially apparent at that time due to the culminating air pollution situation. The alterations of the patina on bronze sculptures during the industrial epoch had changed not only the apprehension of what was a desirable patina, but also the conception of what was natural. Now the *green, patchy and streaked* appearance of bronze sculptures became recognized as a problem in some parts of the world, while another approach maintained the romantic vision that copper turns "naturally" green and implied waiting for this to occur.

Since the 1970s, activities have increased and diverse approaches to conservation have been practised. Predominant attitudes of *professional categories* involved have influenced on the view of the pollution-induced appearance, as well as on the dominant approaches to conservation. Moreover, different climatic conditions and air pollution situations have caused various appearances of sculptures in specific places. As *continuity* is an essential emotional aspect in reactions to outdoor art-works, it is reflected in attitudes to alterations occurring on sculptures and the conservation approaches chosen.

Outdoor public sculpture presents a wide variety of objects that resides in different characteristic, mainly being conceived as *works of art* but *also having other meanings.* One of the major problems regarding conservation seems to be connected with the *complex nature* of these art-works and the difficulty of formulating an unambiguous approach. Therefore, values assigned to each single object should be identified in order to preserve and respect the essential message of a sculpture. As the judgements of these values may differ among groups of people and individuals, respect for the values should be considered within the context to which the sculpture belongs. The properties of an object that are favoured by decay, conservation or restoration interventions should also be considered with a *sound knowledge of the effects of time* and treatments of the object. Moreover, future work should be based on the accumulated knowledge of previous experiences and mistakes.

The *general care and maintenance* of outdoor sculptures has been and still is largely neglected. However, the tendency within bronze sculpture conservation promisingly seems to indicate *preventive conservation, maintenance plans* and minimal and *retreatable* intervention performances, abandoning strong measures such as stylistic restoration.

3 METHODOLOGY

This dissertation is mainly based on laboratory research. However, case studies of outdoor bronze sculptures have also been carried out to determine their state of preservation and to elucidate deterioration processes in the corrosive outdoor environment. The laboratory investigations have focused on the mechanisms of the atmospheric corrosion of copper, bronze and patina constituents. Samples have been exposed in synthetic atmospheres to elucidate crucial factors affecting corrosion. Some properties of corrosion products have also been investigated; moreover, the structural determination of a novel corrosion product has been performed.

3.1 Case studies

The state of preservation of some outdoor bronze sculptures was examined.[132] Fourteen sculptures from 1869-1991 located in Göteborg were selected to illustrate the variation in appearance of the patina, reflecting different states of preservation, due partly to the varying age of the sculptures, but also to other factors such as alloy composition, original patination method and location. By selecting sculptures of different ages an attempt was made to describe the stages of degradation in this respect. The majority of the objects was younger than 50 years.

The sculptures were visually inspected and documented by photography. Characteristic features of the patina, such as light and dark areas and streaks, were registered. The stratified structure of corrosion products in the patina was recorded, regarding the colour and thickness of layers, and was schematically sketched. Patina samples were taken from a few selected characteristic parts of the sculptures. They were collected by scraping a small area (0.5-1 cm^2) on the patina with a scalpel, transferring a small amount directly to an adhesive tape. Crystalline compounds were identified by X-ray diffraction (XRD) using the Guinier camera technique and a computerized photo-scanning system (section 3.2.4).

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[132] This investigation is reported in Strandberg and Rosvall, 1994, and a summary of the results is presented in **Paper II** appended to this thesis.

To describe the stage of deterioration of a sculpture it is necessary to know the original appearance of the object. Studies of archives and interviews were conducted to obtain such information. The original appearance could be indicated by studies of historical photographs, and by comments in newspapers at the time of inauguration of the sculpture. Bronze sculptures located indoors in museums, protected from the corrosive outdoor environment, were also a source for comparative studies. Moreover, craftsmen working with casting, chiselling and patination have invaluable knowledge in this field which seldom has been documented. The artists' intentions and evaluations of the visual changes of sculptures by time were discussed with artists, relatives of artists, and the public.

3.2 Laboratory exposures

Laboratory exposures of samples were performed in synthetic atmospheres to contribute to the understanding of deterioration processes occurring in the outdoor environment. In a specially developed experimental setup (Figs. 3.1 and 3.2) mechanistic studies were performed to elucidate the effects of trace gases, such as SO_2, NO_2 and O_3, on e.g. copper, bronze, and patina compounds identified in aged patina layers. The main advantage of the equipment is the high control and accuracy in regulation of temperature, gas flows, relative humidity, and concentrations of corrosive gases. The concentrations

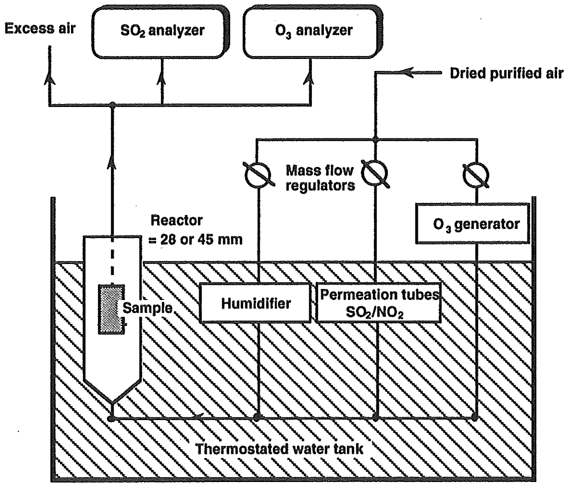

Fig. 3.1 Experimental setup for on-line studies of SO_2 deposition.

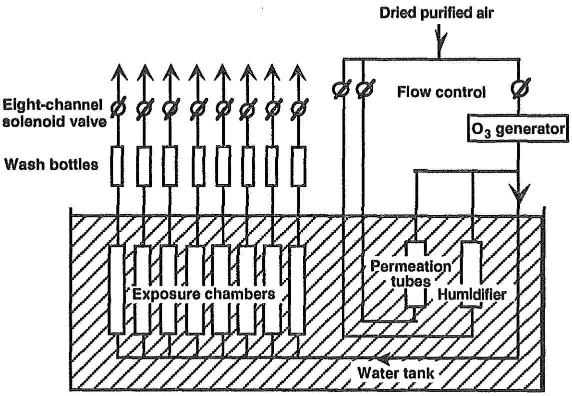

Fig. 3.2 The corrosion exposure system for studies of atmospheric corrosion in synthetic environments.

of air-pollutants in the laboratory studies performed ranged between levels present in rural atmospheres up to concentrations occurring in heavily polluted environments (compare with section 6). The relatively high pollutant concentrations were used to obtain measurable corrosion rates. Pollutant levels are still considered to be realistic, however.

Below, a summary of the experimental conditions is presented. Detailed descriptions about experimental setups, analytical techniques, and calculations performed can be found in the appended papers.

3.2.1 Materials investigated

Metal plates

The copper material used[133] was oxygen-containing cold-rolled 1/2-hard copper sheet metal (1.25 mm, ISO Cu-FRTP) with a minimum copper content of 99.85%. This material is in common use for roofing, facing, furnishings, light fittings and tanks.

In one investigation,[134] three cast statue bronze alloys with elemental compositions described in Table 4.1 were exposed in corrosive atmospheres. For one of these alloys (Josef II), two different microstructures were studied, one bronze material being chillcast

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[133] Paper III-V.

[134] Paper VI.

while the other was tempered. In this investigation, some studies were also carried out on samples made from the pure alloying constituents, copper, tin, zinc and lead (Cu >99.85%, Sn 99.9985%, Zn >99.9%, Pb 99.94%).

Plates were cut to shape and a hole was drilled in each for suspending the sample by a nylon thread. The samples were polished in ethanol with SiC paper to 1000 mesh. The plates were then cleaned in 99.5% ethanol using ultrasonic agitation and rinsed before drying at room temperature. The final geometrical area was 20 cm^2 for the pure metals and 15 cm^2 for the bronze samples. The samples were stored in a desiccator over silica gel (<1% RH) before and after exposure.

Preparation of patina compounds

Powdered samples of the copper patina compounds cuprite, tenorite, antlerite, brochantite, atacamite/clinoatacamite and $Cu_{2.5}(OH)_3SO_4 \cdot 2H_2O$ were used in the experiments.[135] Cuprite (Riedel-de Haen Ag.) and tenorite (Merck p. a.) were used as received while the copper hydroxy compounds were synthesized from analytical grade reagents.

Antlerite ($Cu_3(OH)_4SO_4$) was prepared by dropwise addition of a solution of 11 g $NaHCO_3$ in 100 ml water to a boiling solution of 83 g $CuSO_4 \cdot 5H_2O$ in 500 ml water. The slurry was then refluxed for 15 hours. The precipitate was collected on a sintered glass filter no. 3, applying suction. The product was washed with water and 99.5% ethanol and dried with suction. Finally, the compound was dried at 100°C.

In order to prepare brochantite ($Cu_4(OH)_6SO_4$), 40 g CuO was treated with a solution of 200 g $CuSO_4 \cdot 5H_2O$ in 4 l water. The slurry was mixed at room temperature in a round-bottomed flask using a magnetic stirrer. After two weeks' agitation the precipitate was collected, washed and dried as above.

The copper hydroxy chloride dimorphs atacamite and clinoatacamite ($Cu_2(OH)_3Cl$) were prepared as a mixture. In the effort to synthesize the pure compounds, atacamite formed mainly at room temperature, but as a flocculent precipitate that was difficult to filtrate. Elevating the temperature to 100°C resulted in the formation of pure clinoatacamite in the form of large crystals. Therefore, a mixture of atacamite and clinoatacamite was prepared by treating 25 g CuO in a solution of 90 g $CuCl_2 \cdot 2H_2O$ in 4 l water heated to 35-40°C. The slurry was mixed using a magnetic stirrer in a round-bottomed flask for 24 hours. The precipitate was collected and washed as above. The compound was dried at 40°C.

$Cu_{2.5}(OH)_3SO_4 \cdot 2H_2O$ was prepared by treating CuO in a saturated solution of $CuSO_4 \cdot 5H_2O$ at room temperature. 1 g CuO and 10 g of $CuSO_4 \cdot 5H_2O$ were mixed in a 50 ml round-bottomed flask, and 5 ml of high purity water was added slowly to the

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[135] **Paper I, VII and VIII.**

mixture. After 24 hours of agitation using a magnetic stirrer, the product was collected and washed as above. Finally it was dried in vacuum over silica gel.

The BET-N_2 surface areas of the patina compounds were 1.99 m^2/g cuprite, 10.27 m^2/g tenorite, 2.15 m^2/g antlerite, 9.12 m^2/g brochantite, and 4.03 m^2/g atacamite/clinoatacamite. In the deposition studies 1 m^2 active surface of the patina compound was exposed corresponding to 0.502 g cuprite, 0.097 g tenorite, 0.465 g antlerite, 0.110 g brochantite and 0.248 g atacamite/clinoatacamite. The samples were stored dry in a desiccator over silica gel (<1% RH) before and after exposure.

Pretreatment of samples with NaCl and active carbon

The influence of NaCl on the atmospheric corrosion of copper and patina compounds was studied by treating samples with salt before the experiments.[136]

The treatment for the metal plates consisted of spraying the samples with 90% ethanol solution saturated with NaCl. After drying by air and storing dry in desiccator, the amount deposited was determined gravimetrically.

Patina compounds were mixed with 10wt% NaCl. A measured volume of NaCl solution (8 g/100 ml H_2O) was added and rapidly stirred with the compound (~10 s), and the mixture was then dried in vacuum at room temperature (less than 5 minutes). Cuprite and tenorite did not react noticeably with NaCl during pretreatment. Antlerite and brochantite, however, reacted quantitatively during the brief mixing with NaCl in water, and no NaCl remained after the pretreatment. Antlerite formed atacamite, clinoatacamite, and the third copper hydroxy chloride polymorph botallackite ($Cu_2(OH)_3Cl$), which is known to be metastable with respect to the other two. Brochantite formed atacamite.

Cuprite and tenorite were also pretreated with 10wt% active carbon.[137] The carbon was obtained from a commercial supplier and ground to a particle fraction with a size range of 10-50 µm. A mixture of 10% carbon and 90% copper oxide was obtained by stirring the dry powders.

Treatment with protective coatings

In a pilot study protective coatings for bronze sculptures were tested on polished copper samples.[138] The conservation products were: polyethene wax, microcrystalline wax, paraffin wax and Incra lacquer. The conservation products were dispersed and applied to polished copper samples by a brush. The samples were dried in ambient air for two weeks before the exposures were started.

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[136] **Paper V and VIII.**

[137] **Paper VII.**

[138] Results are presented in Appendix 2.

3.2.2 *Experimental setup*

The experiments were carried out using two different experimental setups (Figs. 3.1 and 3.2). All equipment was made of glass and Teflon and was immersed in a water tank kept at 22.00±0.03°C. The temperature in the room was kept at 23-25°C to avoid condensation in the parts of the system outside the water tank. The room was kept enlightened during day and night. The first part of the system was the same for both experimental setups and consisted of an air purification and drying system, the clean and dry air entering the apparatus in two flows. One air flow passed through the humidifier in which the air was saturated with water vapour at 22.00°C. The other air flow was dry and was used as a carrier for the trace gases. SO_2 was added from thermostated permeation tubes containing the liquefied gas. O_3 was produced by an O_3 generator using UV radiation (λ<230 nm). The total gas flow and the relative humidity were controlled by mixing measured amounts of dry and humidified air. Relative humidity was controlled with an accuracy of ±0.3% RH.

Deposition studies

In the apparatus for the short-term (20 hours) deposition experiments (Fig. 3.1), a continuous flow of the corrosive humidified gas passed through the reaction cell. In the case of a metal plate the sample was suspended by a nylon string, the gas flowing parallel to the sample. The diameter of the cell was 45 mm in the experiments involving the pure metals and 28 mm in the experiments with the bronzes or the patina compounds. The gas flow was 1 l/min, resulting in a gas velocity of 10.5 mm/s and 27 mm/s, respectively. In case of a powder, the exposure cell contained a glass filter (Duran, porosity 16-40 µm) mounted perpendicular to the direction of flow. The powder was placed on top of the glass filter, the air flowing through the sample from above. 1 m^2 active surface of the compound was exposed during 20 hours.

The SO_2 concentration in the gas emanating from the exposure cell was analyzed continuously using a fluorescence instrument (Environnement AF 21M, sensitivity 1 ppb). The amount of SO_2 deposited was calculated from the difference between the input and output concentrations. O_3 concentration was monitored with an UV photometric analyzer (Dasibi 1108, 1 ppb detection limit).

Corrosion studies

The corrosion exposure system used for metal plates in the four-week studies is shown in Fig. 3.2. In this setup the corrosive humidified gas passed through eight parallel corrosion chambers, each with a volume of 0.4 l and an inner diameter of 55 mm. Each sample was exposed in a chamber of its own. To obtain equal gas flow in all chambers, a multichannel solenoid valve distributed the gas sequentially among the exposure chambers, the whole gas flow passing each chamber in turn for 37.5 seconds. The rate of gas flow was 1 l/min being equal to a gas velocity of 7 mm/s each time a chamber was open.

In the four-week experiments exposing powdered samples, four to eight exposure chambers were connected in series. Since very small amounts of material were exposed in each chamber (~10 mg), concentration levels and relative humidity were not considered to be influenced appreciably. The pressure drop due to the glass filter beds was negligible (<0.1%).

3.2.3 *The corrosive atmospheres*

An advantage of the experimental setup described is the possibility to use pollutant concentrations of the same order of magnitude as in outdoor air (compare with section 6). However, to reach corrosion rates giving measurable amounts of corrosion products during the four-week exposures, the concentration levels were usually higher than what is found in moderately polluted urban air. Thus, the pollutant concentrations in the laboratory exposures often resembled heavily polluted urban air (see Table 6.1).

Exposures were usually performed at 90% RH, and in some cases at humidities ranging from 0-99% RH. The corrosive atmospheres contained SO_2, NO_2 or O_3, separately or in the combination of SO_2+O_3 or SO_2+NO_2. Concentrations of air-pollutants were usually about 500 ppb, but varied in the range 4 to 1000 ppb in some of the studies.

3.2.4 *Qualitative analysis of corrosion products*

XRD

X-ray powder diffraction (XRD) was used to identify crystalline phases in corrosion products.[139] Corroded metal plates were analyzed in a Siemens D 5000 θ–θ diffractometer in Bragg-Brentano geometry with Cu $K_{\alpha 1}$ radiation (λ=1.54056 Å). The technique is non-destructive and plates of maximum size 5 x 2 cm may be analyzed. A position-sensitive detector (PSD) was used for fast scans (10 min) of thick corrosion layers, analyzing all corrosion products down to the metal surface. The surface-sensitive grazing-incidence angle (0.5°) technique was used to detect corrosion products in thin corrosion layers or in the surface layers of thicker corrosion layers (<10 nm).

The Guinier camera technique and a computerized photo-scanning system were used for powdered samples. This technique is suitable for small amounts of sample material.

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[139] **Paper I-VIII.**

The samples were exposed to X-rays for approximately eight hours to obtain strong reflections. On several occasions weak and diffuse diffraction lines, visible only to the naked eye, were added to the data set obtained by the photo-scanner.

FT-IR

Non-crystalline compounds could be observed by FT-IR. IR spectra were recorded with a Perkin-Elmer 1800 Fourier Transform Infrared Spectrometer. For powders the KBr pellet technique was used, and for studies of metal surfaces spectra were obtained using Fourier Transform Infrared Reflection Absorption Spectroscopy (FT-IRAS).

XPS

X-ray Photoelectron Spectroscopy (XPS) is a surface-sensitive technique providing information on elemental composition and oxidation states. XPS was used to study thin corrosion layers (1-5 nm in depth) on exposed copper plates, and for characterization of some copper hydroxy sulfates.[140] A PHI 5500 instrument with a monochromatic X-ray source AlK_α (1486.6 eV) was used for metal samples. For powders an MgK_α (1256 eV) anode was used causing less charging of the samples. Multiplex scans were performed for high-resolution information on S(2p), C(1s), O(1s) and Cu(2p). The separation of the two photoelectron peaks $2p_{1/2}$ and $2p_{3/2}$ of sulfur was determined by analyzing the spectrum of pyrite (FeS_2) and was found to be 1.2 eV.

EPMA

The morphology and the distribution of elements on corroded bronze plates were studied by Electron Probe Micro Analysis (EPMA).[141] Three types of images were displayed. Secondary electron images (SEI) mainly indicated the morphology but were also sensitive to the atomic number. Back-scattered electron images (BEI) revealed parts of the surface enriched in elements of high atomic numbers. X-ray mapping was performed to study the distribution of specific elements.

3.2.5 Quantitative analysis of corrosion products

Analysis for sulfite

Some copper samples were analyzed for sulfite.[142] A three-necked round-bottom flask made of glass containing 40 ml 1 M $HClO_4(aq)$ replaced the corrosion chamber in Fig. 3.1. The exposed sample was immersed in the perchloric acid, causing the following reactions:

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[140] **Paper III** and Appendix 1.

[141] **Paper VI.**

[142] **Paper III.**

$SO_3^{2-} + H^+ \rightarrow HSO_3^-$ [1]

$HSO_3^- + H^+ \rightarrow SO_2(aq) + H_2O$ [2]

$SO_2(aq) \rightarrow SO_2(g)$ [3]

The $SO_2(g)$ evolved was carried to the fluorescence SO_2 analyzer by a stream of purified air. Knowing the rate of air flow, the amount of sulfite on the copper surface was calculated by integrating the output signal from the SO_2 analyzer.

Leaching and pickling

After the four-week experiments, the amount of corrosion products was determined by leaching and pickling the samples in 50 ml solutions at room temperature.[143] First, the easily soluble corrosion products were removed by leaching in pure water (pH 7). In the next step of the leaching procedure sparingly soluble copper hydroxy compounds were removed by immersing the samples in dilute $HClO_4$ solution (pH 2). The next step was pickling in 5% amidosulfonic acid to dissolve the residual corrosion products, i.e. cuprite. Ultrasonic agitation was used in all steps. All aqueous solutions were deareated with N_2 before and during leaching and pickling to control pH by removing CO_2, to stir the solution and to avoid corrosion of the copper sample. The procedure was as follows:

1. Milli-Q water, pH 7
2. 10 mM $HClO_4$, pH 2
3. Pickling in 5% aqueous amidosulfonic acid
4. Milli-Q water
5. 99.5% ethanol

IC

The first two leaching solutions (pH 7 and pH 2) were analyzed for sulfate and chloride by Ion Chromatography (IC) using a Dionex DX-100 instrument with an IonPac column.

3.2.6 Calculations of corrosion product composition

Based on the IC analysis, metal loss data and the composition of the relevant compounds, the mass of each corrosion product was calculated.[144] The metal loss

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[143] **Paper IV-V.**

[144] **Paper IV-V.**

was calculated by weighing the sample before the corrosion exposure and after the leaching and pickling procedure. The mass of dry corrosion products was calculated as the difference between the dry weight of the samples after exposure and the weight after pickling.

3.3 Structure determination of a novel corrosion product

In the course of the laboratory studies of atmospheric corrosion, products with X-ray diffraction patterns that did not belong to known compounds were identified.

$Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$ was successfully synthesized as a pure product and it was subjected to a full structure determination.[145] The preparation of the powder is described in section 3.2.1. In order to prepare crystals of sufficient size and quality for single-crystal determination an alternative method was used. A piece of copper sheet which had been oxidized to form tenorite on its surface was covered with $CuSO_4{\cdot}5H_2O(s)$ and was exposed to air at approximately 100% RH at room temperature. After several months' exposure, minute quantities of greenish crystals with maximum dimensions of 0.03 mm had formed. One of these crystals was selected for the single-crystal work. The measurements were performed on a Rigaku AFC6R diffractometer with graphite monochromated Mo K_α radiation and a 12 kW rotating-anode generator.

Another unknown corrosion product (working name phase II) was identified on samples pretreated with NaCl exposed in humid air containing SO_2.[146] Efforts have been carried out to synthesize this compound, but it has not yet appeared as a pure product. This phase remains to be determined in future work.

3.4 Some properties of copper patina compounds

XPS analysis of antlerite, brochantite and $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$ were performed as described in section 3.2.4. Multiplex scans for high-resolution information on S(2p), O(1s) and Cu(2p) were obtained.[147]

The formation of $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$ and other hydroxy sulfates was studied during varying experimental conditions using XRD.[148]

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[145] **Paper I.**

[146] **Paper V and VIII.**

[147] Appendix 1.

[148] Appendix 1.

4 COPPER AND BRONZE MATERIAL

4.1 The use of copper as building material

Copper has a very long tradition as an architectural material which probably dates back to the 13th century. In Scandinavia the use of copper roofs on castles and churches has been mentioned since the 16th century. An increased production occurred during the 19th century due to the new technique of rolling sheet-metal instead of the previous hammering, and this sheet-metal became widely used as building material not only for castles and churches, but for all kinds of buildings. Towers, spires, domes, and other decoration elements attributed to the style of the epoch were easily covered with the thin metal sheets and carried a certain cachet to the building. At the turn of the century, the stylish design of roofs on residential houses favoured the use of sheet-metal, as did the roofs on public buildings in the modern style. Other copper-alloy materials have also found applications on buildings. Copper has been highly appreciated as building material, considered to be durable and corrosion-resistant with good ageing characteristics, and has not demanded general maintenance.[149]

4.2 Sculptures in bronze

4.2.1 The casting of bronze sculptures

Bronze casting has an old tradition originating from prehistory. The methods of production have remained principally the same since the early phase, until very recent decades. Thus, since the 1950s, parts of sculptures began to be joined by argon-welding instead of being joined mechanically with pins. This implied that large sculptures could be cast in smaller pieces that were easily assembled.[150]

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[149] Mattsson and Holm, 1964; Mattsson and Holm, 1968; Gudmunsson, 1989; Folmer, 1997, unpubl.
[150] Strandberg and Rosvall, 1994; Gullman and Törnblom, 1994, pp. 15-24.

There are two principal methods of casting sculptures, "cire perdue" (lost wax) and sand-casting. These techniques are described elsewhere.[151] "Cire perdue" is the oldest method and was used already several thousand years ago. It is the most delicate method and may give the finest details in the surface with no fins visible after casting. In the 17th-18th centuries big equestrian statues were cast by this method, some even cast in one piece only. Nowadays the technique is used only by a few foundries, mainly for small objects (less than 1.5 m).[152]

Sand-casting in large scale was introduced during the industrialism at the end of the 18th century, having its source in England. In the 19th century, casting with cire-perdue technique belonged to the Italian and French schools, while sand-casting was the prevalent technique in Germany. Most outdoor sculptures are sand-cast since the process is easier to control and includes less risky steps. However, this technique requires more work before the sculpture is finished. Solidified metal in fins between the pieces of mould and metal in air vents are cut away by sawing, filing or grinding and the surface is made smooth by chasing and polishing.[153]

Large sculptures are constructed with an iron skeleton serving as an inner armature for the core, while smaller sculptures occasionally require reinforcement in some weak parts.

4.2.2 Material and microstructure

Bronze used for sculptures usually contains 1-10% tin, 1-10% zinc, and 0-6% lead, the major part being copper.[154] Tin and zinc increase breaking strength and hardness while zinc and lead increase pourability.[155] The composition of the alloys used through the ages has varied a lot, due partly to taste, but also to the availability of various metals and to the frequent use of scrap-metal with unidentified composition.[156]

Table 4.1 displays approximate alloy compositions of some bronze monuments in Europe from the last century. A commercial bronze alloy frequently used nowadays is Rg 5 which is quite high in lead and contains: 85% Cu, 5% Sn, 5% Zn, and 5% Pb. Other commercial alloys for bronze casting are Rg 7 (83% Cu, 7% Sn, 4% Zn, 6% Pb); Rg 9

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[151] Holm, 1981; Lins, 1983; Rådström, 1989; Gullman and Törnblom, 1994, pp. 15-24; Refsum, 1996.

[152] Holm, 1981; Lins, 1983; Rådström, 1989.

[153] Lins, 1983; Minne and Bergqvist, 1993, unpubl.; Gullman and Törnblom, 1994, pp. 15-24.

[154] Riederer, 1972; Jenssen, 1986, unpubl.; Minne and Bergqvist, 1993, unpubl.

[155] Gullman and Törnblom, 1994, p. 24.

[156] Minne and Bergqvist, 1993, unpubl.

(85% Cu, 9% Sn, 4% Zn, 2% Zn); Tb 10 (90% Cu, 10% Sn) and a bronze high in zinc (86% Cu, 2% Sn, 10% Zn, 2% Pb).[157]

Table 4.1 Alloy composition of some statue bronzes from the last century, investigated within the Eurocare-Copal project. From **Paper VI** and Pichler *et al.*, 1994.

Monument	Place (inauguration)	Composition % Cu	Sn	Zn	Pb	Fe, Ni, Ag, Sb, As
Gustav II Adolf	Göteborg (1854)	90.9	5.9	0.6	2.0	0.6
Josef II	Vienna (1795-1807)	93.0	1.4	4.9	0.4	0.3
Max II	Munich (1875)	83.6	4.5	5.6	5.5	0.8

When a tin bronze is cast, the alloy is extensively segregated, usually with a dendritic crystal growth, and an infill of $\alpha+\delta$ etectoid surrounding the dendritic arms. The centers of the arms are copper-rich, since copper has the higher melting point, while the successive solidification results in the deposition of more tin. At low tin content, i.e. below 5%, it may be possible for all the tin to be absorbed into the dendritic growth, especially if the cooling rate is slow and accordingly the possibility to reach equilibrium is greater. Lead is insoluble in the alloy and occurs as small globules throughout the structure. Distribution is generally fine and random, but some gravity segregation may cause accumulation at the bottom of the castings (Fig. 4.1).[158]

The parts of the bronze which solidify first have different structure and alloy composition compared to those that solidify last. When the metal initially hits the cold mould, it forms a fine-grained homogeneous layer, i.e. a chilled layer. As solidification continues, larger crystal dendrites are formed in the body of the casting. Copper is enriched in the parts of the sculpture where the alloy solidifies first, while tin and lead are enriched in the parts where the alloy solidifies last. Porosity in the bronze is caused by gas evolved during solidification.[159]

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[157] Jenssen, 1986, unpubl.; Minne and Bergqvist, 1993, unpubl.; Lindahl, 1993, unpubl. The Scandinavian designation Rg means "Rödgods". The bronze alloy containing 10% zinc is named "konstbrons". Today the alloys containing high amounts of zinc and lead are avoided due to their health hazard.

[158] Scott, 1991. In **Paper VI** the segregated structure of a low-tin bronze is shown.

[159] Naudé, 1983c, pp. 78-83; Ammannati *et al.*, 1992.

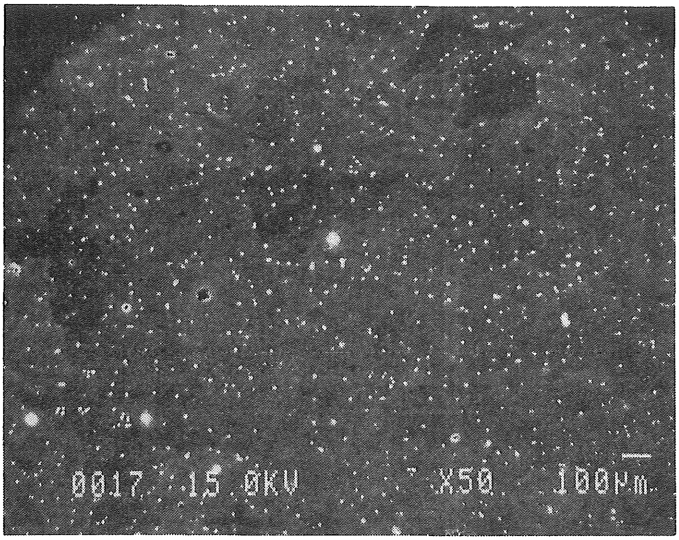

Fig. 4.1 EPMA-photo (BEI-image) of a segregated chillcast bronze material with dendrites of a solid solution (Josef II bronze: 1.4% Sn, 4.9% Zn, 0.4% Pb). Globules of lead are visible as white spots. Tin is enriched in the remaining melt around the lead globules. Additional EPMA-photos are presented in **Paper VI**.

4.2.3 Artificial patination

Patination of sculptures is of great significance since it is the process that provides final visual coherence to a piece, and ultimately articulates the surface qualities. The patina produced on bronze sculptures is often the result of a collaborative work between the artist and the foundry. The range of qualities includes a great variety of surface effects. The degree of translucence or opacity, the layers of colours in the patinated surface, the degree to which the colour is controlled or relieved to achieve modulation of form, and the mattness or glossiness of the surface are among the many variable qualities creating the visual totality of an individual work of sculpture.[160]

Bronze sculptures have always been artificially patinated with chemicals and heat, making use of the corrosion process, to produce a great variety of qualities. The historical development[161] and diverse techniques[162] of artificial patination have been described elsewhere.

It often occurs that bronze sculptures have been artificially patinated with sulfur compounds, e.g. liver of sulfur ($K_xS+K_2S_2O_3$) or ammonium sulfide ($NH_4HS(aq)$), thereby achieving a deeper brownish shade due to the formation of copper sulfides (see

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[160] Hughes and Rowe, 1983; Hughes, 1992.

[161] Weil, 1977.

[162] Hughes and Rowe, 1983; Hughes, 1992.

Fig. 4.2). This kind of patina is usually thin and transparent permitting the metallic lustre to reflect the light, but may also be darker when the metal is heated during patination. Copper sulfate, nitrate, and chloride, strong mineral acids, ammonium chloride, zinc and iron compounds, etc. have been used to obtain green and other colours of patina. Many sculptures have been placed outdoors without patination, exhibiting the shiny bronze colour.[163]

The quality of the casting may determine the method of patination chosen. Green patination has occasionally been used by sculptors attempting to conceal bad workmanship.[164]

Sculptures have often been surface-treated with wax before leaving the foundry. Natural and synthetic waxes have been commonly used. Linseed oil and shellac are also known to have been applied in the past. Occasionally, recent sculptures have been sprayed with silicone spray in the foundry.[165]

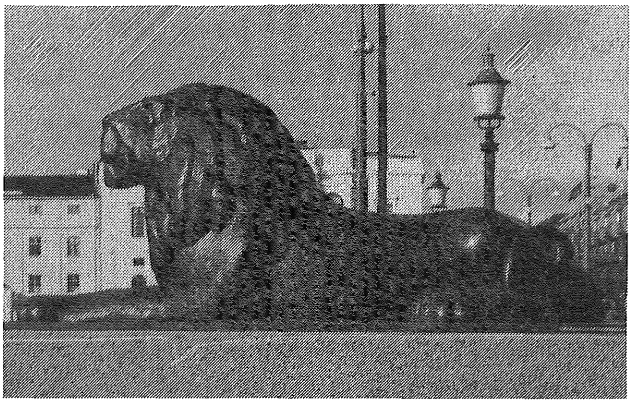

Fig 4.2 Bronze lion ("Lejon") by Camilla Bergman, after two years' outdoor exposure in central Göteborg. The sculpture was originally patinated with ammonium sulfide, and surface-treated with beeswax before the inauguration in 1991. From Strandberg *et al.*, 1994. Photo 1993: Helena Strandberg.

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[163] Strandberg, 1986; Strandberg and Rosvall, 1994; Gullman and Törnblom, 1994, pp. 83-157.

[164] Hughes and Rowe, 1983.

[165] Lins, 1983; Minne and Bergqvist, 1993, unpubl.; Selwyn *et al.*, 1996.

5 THE CONDITION OF OUTDOOR COPPER AND BRONZE

Copper and bronze objects develop patina layers that gradually change with time in the corrosive outdoor environment. In the assessment of the physical condition of bronze sculptures and copper roofs, a range of factors may be taken into consideration, e.g. alterations in the visual appearance; formation of disfiguring corrosion crusts, patches and streaks; pitting corrosion of the alloy; deposition of corrosive substances; composition of the patina (e.g. formation of soluble or insoluble compounds); and weathering of patina compounds. The variation in condition depends on e.g. bronze alloy, original patination method, age of the sculpture, the location, different kinds of areas on the sculpture, e.g. rain-exposed or rain-sheltered areas, etc.

This section is primarily based on observations made on bronze sculptures in Göteborg and Copenhagen.[166] The comparisons with other authors' reports are indicated by footnotes.

5.1 Visual appearance of bronze sculptures

5.1.1 General appearance

Many sculptures have originally been artificially patinated, e.g. to achieve a deep brownish shade. This patina usually is thin, the metallic lustre reflecting the light (see e.g. Fig. 4.2). After a few years of outdoor exposure, copper and bronze turn a darker brownish shade and a greenish hue may become discernible.[167] At closer inspection the green corrosion products are most evident in small depressions in the bronze surface, e.g. where the surface has been tooled.

After some decades' exposure a patchy and streaked appearance with alternating black and light green areas tends to develop on copper and bronze. Rain-washed areas tend to be light green, while areas sheltered from the rain tend to be black. Vertical light green streaks appear where rain water is drained in rivulets.

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[166] **Paper II**; Strandberg, 1986; Strandberg and Rosvall, 1994.

[167] Holm and Mattsson, 1982.

In Göteborg, the sculptures from the 1940s and 1950s appeared to be in a considerably worse condition than the sculptures from a later period (see Figs. 5.1, 5.2, 5.3 and 5.4). They showed evident contrasts between dark and light green areas and distinct vertical streaks. Orange or brown areas also occurred indicating the leaching of an area previously dark. However, the appearance of the sculptures from this period varied quite a lot, some being principally dark and others being light green. Thus, it seems that patina on sculptures from this period is now in a state of rapid change. In accordance with this, the sculptures in the Vigeland Park in Oslo, inaugurated in the 1940s, exhibited a sudden change in appearance in the 1970s. A bluish shade on the previous brown patina was observed.[168] The present appearance resembles sculptures from the same decade in Göteborg and in Copenhagen.

Older sculptures, from the 19th century or from the beginning of this century, exhibited considerably thicker corrosion product layers than later sculptures (Fig. 5.5). In some cases the sculptures appeared predominantly green. Horizontal rain-exposed parts of the light green areas were consistently more deteriorated than other areas having a pitted appearance where the "original surface" was partly or completely destroyed (compare sketches in Fig. 5.6). The weathering process was obvious on these parts of the patina. The green discoloration on adjacent stone bases of older sculptures, also indicate the dissolution and washing-out of copper compounds. Thick black hard crusts are evident in rain-sheltered areas. Tool marks may be observed in the black areas, in smooth areas as well as in the coarse raised crust, and to some extent in vertical light green areas.

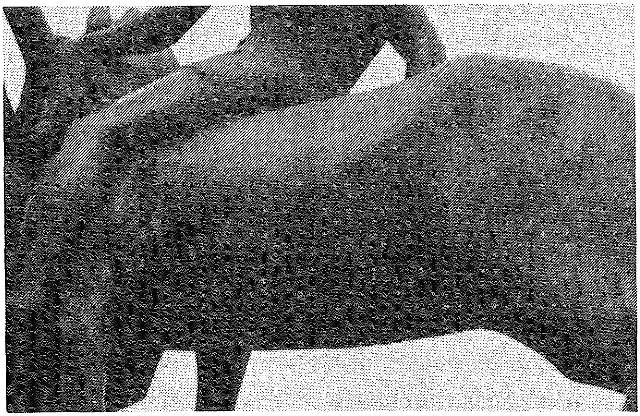

Fig. 5.1 "När vänskapsbanden knytes" by Wäinö Aaltonen in Näckrosdammen park area in Göteborg (inaugurated 1955). Photo: Helena Strandberg 1993.

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[168] Wikborg, 1996, unpubl.

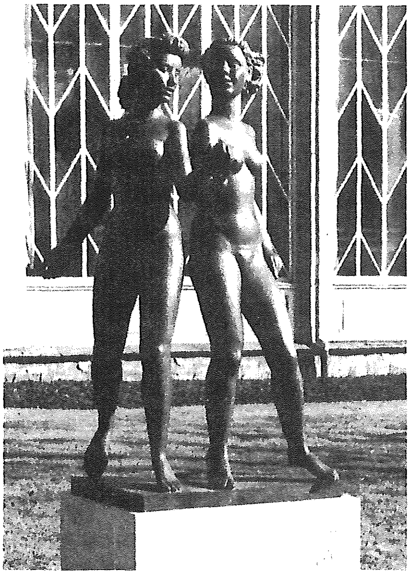

Fig. 5.2 Dance ("Dans") by Axel Wallenberg in Liseberg amusement park in 1953, three years after the inauguration in 1950.
Photo: Archive of the City Museum.

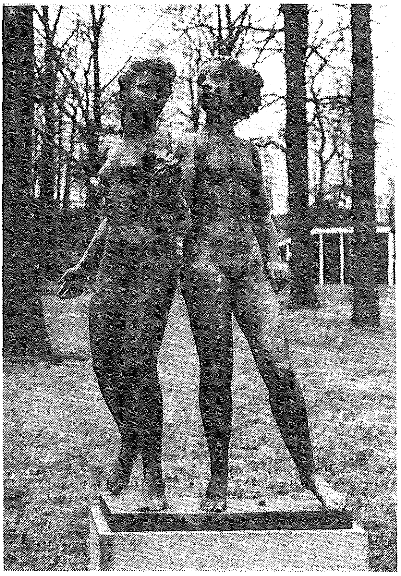

Fig. 5.3 Dance ("Dans") by Axel Wallenberg in Liseberg amusement park in 1993, after 40 years' outdoor exposure (inaugurated 1950). Photo: Helena Strandberg, 1993.

5.1.2 Influence of location

The location of a sculpture is of certain importance for its condition. Objects exposed to strong winds from the sea are characterized by being more light green on this side (Fig. 5.5).[169] Sculptures in parks sheltered from wind and traffic are reported to be better preserved than objects exposed to heavy traffic.[170]

5.1.3 Influence of artificial patination

The appearance of sculptures may vary quite a lot due to the original artificial patination method used. It should be noted, however, that traces of the compounds (e.g. sulfides, copper nitrate) created during the artificial patination are seldom detected in the patina on a sculpture that has been exposed to the outdoor environment for some decades. In the Göteborg examination, sculptures from the 1940s and 1950s which probably were originally dark-patinated still appeared darker than other bronzes from the same age. On

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[169] **Paper II**; Livingston, 1991.
[170] **Paper II**; Sherwood, 1992.

one of these sculptures, marks probably indicating brush strokes from the patination also appeared in the corrosion product layer (Fig. 5.3). Other characteristic features of originally patinated sculptures may be due to localized corrosion that is suggested to have been caused by a previously rather thick layer of sulfides acting as cathodic areas (see Fig. 5.4). Patchy and cracked patterns on old sculptures may also indicate an original patination or surface treatment.[171] Areas of red cuprite appearing may originate from an artificial patination applied with chemicals and heat.

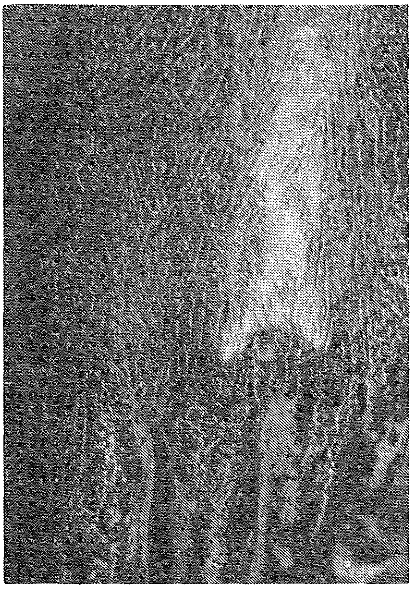

Fig. 5.4 Reclining girl ("Liggande flicka"), left hand, in Copenhagen, by the sculptor Gerard Henning (inaugurated 1945).
Photo: Helena Strandberg, 1986.

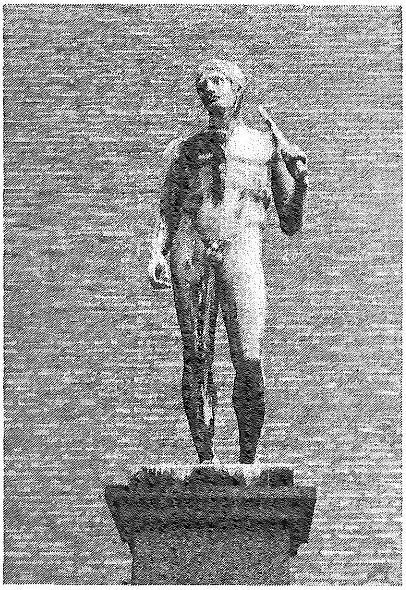

Fig. 5.5 The copy in bronze of the antique sculpture Doryphoros in front of the Museum of Art in Göteborg (inaugurated 1927).
Photo: Helena Strandberg, 1993.

5.1.4 Influence of bird-droppings

Bird-droppings cause obvious corrosion damage on parts of bronze sculptures, due to corrosive compounds dissolving the patina compounds. Greenish disfiguring deposits and streaks are formed indicating that copper is involved. This corrosion phenomenon remains for future research to investigate.

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[171] See e.g. Gullman and Törnblom, 1994, pp. 45-47.

5.2 The composition of outdoor patina

A patina developed over many years contains a number of compounds that together provide the overall appearance (Table 5.1). This includes corrosion products, and deposited material such as aerosol particles, wind-blown dust, soot and bird-droppings. The major copper corrosion products occurring in the patina are cuprite (Cu_2O), the hydroxy sulfates brochantite ($Cu_4(OH)_6SO_4$) and antlerite ($Cu_3(OH)_4SO_4$), and the hydroxy chloride dimorphs ($Cu_2(OH)_3Cl$) atacamite and paratacamite (=clinoatacamite, see below).[172] After shorter exposures, up to ten years, posnjakite ($Cu_4(OH)_6SO_4{\cdot}H_2O$) is recently reported to be a common corrosion product.[173] Additionally, $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$[174] and chalcantite ($CuSO_4{\cdot}5H_2O$)[175] have been identified in outdoor patina. Cuprite and brochantite tend to dominate on rain-washed light green areas, while several compounds, including copper hydroxy chlorides and antlerite, are found in dark rain-sheltered areas.[176]

Table 5.1. Mineral names, formulas and Powder Diffraction File (PDF) numbers of some copper patina compounds occurring on outdoor copper and bronze objects, and of compounds found during laboratory exposures.

Mineral name	Compound	PDF
Cuprite	Cu_2O	5-0667
Tenorite	CuO	41-0254
Brochantite	$Cu_4(OH)_6SO_4$	13-0398, 43-1458
Antlerite	$Cu_3(OH)_4SO_4$	7-0407
Posnjakite	$Cu_4(OH)_6SO_4{\cdot}H_2O$	20-0364
(Not named)	$Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$	resembles 41-0007
Chalcantite	$CuSO_4{\cdot}5H_2O$	11-0646
Bonnatite	$CuSO_4{\cdot}3H_2O$	22-0249
Nantokite	$CuCl$	6-0344
Atacamite	$Cu_2(OH)_3Cl$	25-0269
Clinoatacamite*	$Cu_2(OH)_3Cl$	resembles 25-1427
Botallackite	$Cu_2(OH)_3Cl$	8-0088
Kroehnkite	$Na_2Cu(SO_4)_2{\cdot}2H_2O$	25-0826
Phase II	probably a hydroxy chloride sulfate	not determined
Malachite	$Cu_2(OH)_2CO_3$	41-1390

* Previous reports on paratacamite may probably be attributed to clinoatacamite since the PDF no. 25-1427 for "paratacamite" has been claimed to pertain to impure clinoatacamite; see Jambor *et al.*, 1996.

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[172] **Paper II**; Nassau *et al.*, 1987a; Selwyn *et al.*, 1996.

[173] Nassau *et al.*, 1987a; Odnevall and Leygraf, 1995; Oesch and Heimgartner, 1996.

[174] **Paper II**; Selwyn *et al.*, 1996.

[175] Bernardini *et al.*, 1992: Pichler *et al.*, 1994.

[176] **Paper II**; Selwyn *et al.*, 1996.

Cuprite is the first and most common corrosion product formed on copper and bronze exposed outdoors.[177] It is usually found next to the metal surface[178] and may have a red, orange, brown or black appearance. Occasionally, the layer is very thin and not visible to the naked eye, but in most cases it is detected when scraping close to the metal surface. The oxide, *tenorite* (CuO), is rarely found on outdoor objects.[179] Yet the brownish appearance of outdoor objects, has sometimes, albeit without analytical support, been assigned to tenorite.[180]

Brochantite is often the predominant corrosion product on copper and bronze exposed outdoors for several decades. It generates the appearance of the light green rain-washed areas, but occurs in other parts of the patina as well.[181]

Antlerite is mainly identified in rain-sheltered black areas on sculptures older than several decades.[182] This is supported by reports from the 1930s by Gettens,[183] who identified antlerite on a 40-year-old sculpture, and by Vernon[184] reporting a higher acidity in corrosion products on older sculptures. Antlerite is often found together with copper hydroxy chlorides in the patina.[185]

Posnjakite, found after shorter exposures, has been proposed to be a metastable precursor in brochantite formation, due to its structural similarity.[186]

$Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$ has been identified on outdoor bronzes and is suggested to indicate recent active corrosion since the phase is probably metastable.[187] The compound is suggested to be a precursor in brochantite and antlerite formation.[188] A full structural determination has recently been performed.[189] The XRD pattern resembled a compound previously reported in the PDF no. 41-0007 that probably is attributed to an impure sample of $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$.

The copper hydroxy chloride dimorphs *atacamite and paratacamite (=clinoatacamite*, see below) are mostly found on dark sheltered areas of outdoor objects.[190] They occur in all kinds of environments, in both marine and inland areas. Atacamite is found more frequently on outdoor objects than paratacamite, but they are often found together.[191]

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[177] **Paper II**; Mattsson and Holm, 1968; Riederer, 1977; Selwyn *et al.*, 1996.
[178] Opila, 1987.
[179] Selwyn *et al.*, 1996.
[180] Livingston, 1991.
[181] **Paper II**; Mattsson and Holm, 1968; Riederer, 1977; Selwyn *et al.*, 1996.
[182] **Paper II**; Robbiola *et al.*, 1993; Selwyn *et al.*, 1996.
[183] Gettens, 1933.
[184] Vernon, 1932.
[185] **Paper II.**
[186] Nassau *et al.*, 1987b; Pollard *et al.*, 1992b.
[187] **Papers I-II**; Selwyn *et al.*, 1996.
[188] **Paper VII.**
[189] **Paper I.**
[190] **Paper II**; Holm and Mattsson, 1982; Robbiola *et al.*, 1993; Selwyn *et al.*, 1996.
[191] **Paper II**; Nassau *et al.*, 1987a; Bernardini *et al.*, 1992; Selwyn *et al.*, 1996.

These dimorphs may even be difficult to distinguish if mixed with other corrosion products. Jambor *et al.*[192] have recently reported on clinoatacamite, a new mineral polymorph of $Cu_2(OH)_3Cl$. Thus, three well-defined polymorphs, atacamite, botallackite and clinoatacamite, exist. According to the authors, paratacamite probably does not exist as a pure copper mineral. The published PDF no. 25-1427 differs only slightly from clinoatacamite, and is claimed to pertain mainly to the latter compound. Thus, previous reports on paratacamite can probably be assigned to clinoatacamite.

Organic anions such as *formate, acetate and oxalate* have been found in outdoor patina.[193] Copper and calcium oxalate, mooloite ($CuC_2O_4 \cdot xH_2O$) and weddelite ($CaC_2O_4 \cdot 2H_2O$), have been reported on some sculptures.[194] Besides the copper compounds, *lead sulfate, cassiterite* (SnO_2) and *zincite* (ZnO) are occasionally found in bronze patina.[195]

Quartz (SiO_2) and *feldspar* originating from sand and soil are frequently reported to be embedded in the patina as well as *soot particles* from fuel combustion. *Iron oxides* from corroding armature or dust, and *calcite* ($CaCO_3$) and *gypsum* ($CaSO_4 \cdot 2H_2O$) from core material insufficiently removed, wind blown dust or soil, also occur on some sculptures.[196]

5.3 Characterization of outdoor patina

In an examination of sculptures in Göteborg, characteristic features of the patina were described and classified.[197] The areas were described regarding visual appearance, phase composition, and the thickness and morphology of the patina layer. The results of this investigation are summarized below:

Dark smooth areas (Fig. 5.6a), mainly rain-sheltered, appearing black with a green or brown hue, showed the best condition and best represented the "original surface" on sculptures. Patina samples collected from such areas contained cuprite and atacamite. The dark colour was due to cuprite, to a mixture of cuprite and green corrosion products, or to soot particles deposited on the surface. It has been suggested previously[198] that black areas on outdoor bronzes consist of copper sulfides, but this has not been substantiated. Since sulfides are usually poorly crystalline they may be difficult to detect by XRD. Minor amounts of sulfides detected in the patina may be the remains of a thick artificial

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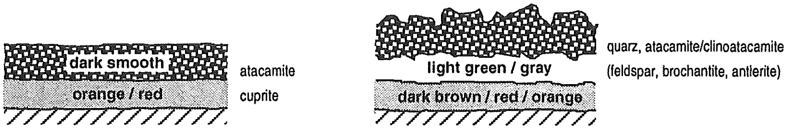
[192] Jambor *et al.*, 1996.
[193] Muller and McCrory-Joy, 1987.
[194] Alunno-Rossetti and Marabelli, 1976; Selwyn *et al.*, 1996.
[195] Selwyn *et al.*, 1996.
[196] **Paper II**; Selwyn *et al.*, 1996.
[197] **Paper II**; Strandberg and Rosvall, 1994.
[198] Lehmann, 1972; Weil *et al.*, 1982.

sulfide patina,[199] or may also be deposited sulfide-containing material, e.g. from tire-rubber.

Black crusts (see Fig. 5.6b), the colour being caused by soot particles, were found on rain sheltered areas of sculptures. These areas exhibit a rough and hard layer that can be peeled off in flakes. Beneath the black crust there was a thin light grey or green layer, and closest to the metal there was a hard smooth dark brown or orange cuprite layer. The black rough crusts always contained quartz and atacamite and/or clinoatacamite. Feldspar, brochantite and antlerite were also present occasionally. Black crusts were generally observed only on sculptures older than four decades.

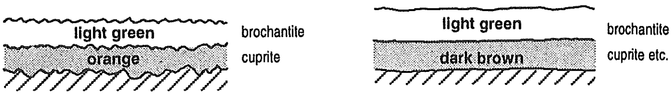
Brown and orange areas consisted of cuprite. A brown patina was observed on the most recent sculptures. Some sculptures from the 1950s showed orange-coloured vertical areas, probably indicating washing-out of green corrosion products by the rain. It seems as though these areas were previously dark, but recently have turned orange revealing the underlying cuprite layer.

Black "islands" were observed surrounded by light green areas that were more heavily etched into the metal. The spots were a few millimetres in diameter, very hard and



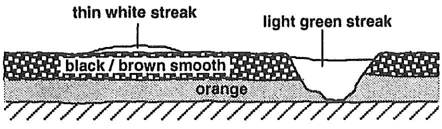
a) Dark smooth area

b) Black crust



c) Horizontal light green area

d) Vertical light green area



e) Streaks on vertical areas

Fig 5.6 Sketches illustrating cross-sections of characteristic patina layers on outdoor sculptures. Results from **Paper II**.

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[199] Selwyn *et al.*, 1996.

very adherent. Such "islands" are probably remaining parts of an earlier black area, for some reason being passivated in the corrosion process. The presence of silicates on shiny "islands"[200] has been reported. Phosphorus compounds have also been found, suggesting pigeons to be involved.[201] Occasionally, these black "islands" have been assigned to copper sulfides.[202] Black particles consisting of tire-rubber from vehicles have also been shown on bronze patina.[203]

Light green areas mainly occurred on horizontal and inclined rain-exposed areas. *Horizontal areas* (Fig. 5.6c) were etched and rough and the patina consisted only of brochantite, and occasionally cuprite from an underlying orange layer. On some sculptures the surface was severely etched and the bare metal was visible. *Vertical areas* (Fig. 5.6d) exposed to strong winds were also light green but contained other corrosion products as well. These areas were not so heavily etched but occasionally had a dark smooth layer closest to the metal. This may indicate the conversion of a previously dark area to green cupric compounds by the influence of e.g. SO_2 and chlorides in the environment. On old sculptures the vertical green areas were thick and smooth in some cases.

Light vertical streaks on darker areas appeared white, grey or light green (Fig. 5.6e). White streaks appeared thin and seemed to lie on top of a smooth dark patina. Light green streaks were more etched down in the patina and a rough thin orange layer or the bare metal was observed beneath.

5.4 Corrosion rates

Copper and bronze have always been regarded as corrosion-resistant materials in outdoor environments. This view is based on the relatively low metal loss as the criterion for assessment. The *durability* for copper roofs, approximately 80-90 years, is largely due to the formation of cracks caused by stresses in the material, but also depends on the quality of the craftsmanship implying that the lifetime may vary considerably, between 5 and 100 years. The use of thinner metal sheets (0.6 mm), and a new technique performed between the 1950s and 1980s, implied a reduction of quality of roofing and decreased the lifetime to some extent.[204]

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[200] Weil, 1974.
[201] Graedel *et al.*, 1987c.
[202] Weil *et al.*, 1982.
[203] Mach and Reinhardt, 1988a.
[204] Hedling, 1997, unpubl.; Sundberg, 1997, unpubl.

Damage on copper sheets caused by atmospheric corrosion is mainly of *local nature*. On certain parts where the fresh and acid rain water is concentrated, e.g. in gutters, corrosion and dissolution of corrosion products may decrease the durability considerably. Rain water falling on copper sheets from plastic roofs, or more severely from bituminous roof material considered to release acids, is also observed to cause damage, the dissolution of corrosion products being evident on exposed parts.[205]

Corrosion rates have been recorded in field exposures of copper and bronze coupons in different environments. Stöckle *et al.*[206] reported the *general corrosion rate* to be higher on copper than on bronze and to be slightly higher on unsheltered samples than on sheltered samples (Table 5.2).

Table 5.2 Mass loss and calculated penetration for copper and bronze samples (Rg 7) exposed at 39 test sites in 14 countries after 1 or 4 years respectively. Stöckle *et al.*, 1993.

Samples	Mass loss after 1 year (mg/cm^2 year)	Mass loss after 4 years (mg/cm^2 year)	Penetration after 4 years (μm/year)
Sheltered copper	0.1-1.7	0.1-1.4	0.1-1.6
Unsheltered copper	0.3-2.8	0.5-2.0	0.6-2.2
Sheltered bronze	0.1-0.7	0.1-1.0	0.1-1.1
Unsheltered bronze	0.3-1.5	0.2-1.6	0.2-1.8

Initially, during the first days of exposure, the corrosion rate may be much higher than shown in Table 5.2, due to large amounts of cuprite forming. A high initial corrosion rate that decreases rapidly with time is often found on copper in exposure sites with low levels of SO_2 and high humidity (e.g. ~1.6 μm/year after one year; and ~0.3 μm/year after eight years).[207] Holm and Mattsson[208] reported the average penetration during 16 years' exposure from various sites in Sweden to be:

0.3 - 0.5 μm/year in rural atmosphere
0.5 - 0.9 μm/year in marine atmosphere
0.9 - 1.3 μm/year in urban atmosphere

Similar corrosion rates have been reported on copper roofs and sculptures in outdoor environments. In an investigation of 200-year-old copper roofs in Copenhagen,

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[205] Hedling, 1997, unpubl.; Outokumpu Copper AB, 1997, unpubl.

[206] Stöckle *et al.*, 1993.

[207] Stöckle *et al.*, 1993; Stöckle *et al.*, 1996.

[208] Holm and Mattsson, 1982.

corrosion rate was reported to have been 1-2 µm/year during the last two centuries.[209]

Pitting corrosion has been measured on some sculptures, indicating pit depths of 5 µm/year, e.g. on a 100-year-old sculpture in Stockholm[210] exhibiting pits with depths of 0.4-0.5 mm, and on a statue in the USA[211] with extreme pitting showing depths up to 0.3 mm after 60 years of exposure.

Considering that copper sheets usually have a thickness of at least 0.6 mm, sheets may be perforated in about 100 years' time by pitting corrosion. Concerning bronze sculptures, casting thickness is several millimetres and the complete conversion of the alloy to corrosion products may not occur in a foreseeable future. The serious problem concerning metal loss is instead the change in surface qualities caused by etching and pitting of the surface, which become prominent even if corrosion is only a few µm.

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[209] Ledheiser, 1979.

[210] Gullman and Törnblom, 1994, p. 127.

[211] Meakin *et al.*, 1992.

6 CORROSIVE ATMOSPHERIC SPECIES – EMISSION TRENDS

6.1 Historical perspective

Human activity has always caused polluted air. Yet emissions were only local problems in previous ages, while nowadays the air pollution situation is recognized as a global problem, caused by the increasing industrialization. The composition of the atmosphere today is strongly affected, not only in urban areas, but also in rural areas far away from the industrialized parts of the world.[212]

Already in Imperial Rome, complaints about smoke were expressed with the increasing urbanization in the capital. The industrial use of coal as a fuel caused public concern during the 13th century in England, due to the hazard to health. In 1661, John Evelyn contributed a book where he directed attention to the industrial sources of air pollution. He argued that the problem arose primarily from the greed of industrialists and could be cured quite simply with their co-operation. Reports about the harmful effects of air-pollutants, on both health and material, were frequent in London during the 17th century. The smoke became an aesthetic concern due to the rapid accumulation of soot, causing dirty exteriors with black crusts. Moreover, stonework and iron were reported to corrode rapidly. The extremely smoky air even influenced the fashions in clothing at the time, and it has also been argued that the umbrella was adopted in England to ward off soot rather than rain.[213]

6.2 Gaseous species

In Table 6.1 typical concentrations of gaseous air-pollutants in different environments are presented. The following sections describe origin and emission trends in a historical perspective for some of the corrosive species.

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[212] Brimblecombe and Rodhe, 1988.

[213] Brimblecombe and Rodhe, 1988.

Table 6.1 Typical concentrations of gaseous air-pollutants in different atmospheres.

Air-pollutant	Concentration (ppb)			
	Remote	Rural	Moderately polluted	Heavily polluted
SO_2*	≤ 1	~1-30	30-200	200-2000
NO_2*	≤ 1	1-20	20-200	200-500
O_3*	≤ 50	20-80	100-200	200-500
HNO_3*	≤ 0.03	~0.1-4	1-10	10-50
H_2S**			0.1-0.5	
Formic acid**			4-20	
Acetic acid**			0.2-1	
HCl**			0.5-2	

* Peak concentrations, 1-hour averages, according to Finlayson-Pitts and Pitts, 1986, pp. 368-369.

** Current concentrations in urban areas according to Graedel, 1987a.

6.2.1 SO_2

The main source for sulfur dioxide in the atmosphere is the combustion of sulfur-containing fossil fuels. Sulfur dioxide is also emitted naturally, e.g. from volcanoes, but this source is smaller than emissions related to human activities.[214]

Historical emission inventories have been compiled over the last several centuries, based on the assumption of coal burning as the major source for SO_2. Total particulate matter and SO_2 concentrations in London were calculated to have gradually increased from the year 1300 to the turn of the 19th century due to the fast expansion of the urban area.[215] In Europe as a whole, total emissions in the period from 1880 to 1990 increased steadily during the first 60 years (Fig. 6.1). A peak in SO_2 concentration occurred at about 1940, followed by a post-war decrease in 1945 and then a rapid increase peaking in the late 1970s. The reduction in the 1980s reflects improvement in the quality of fuel, and refinements in industrial processes, e.g. simple replacement of heavy by light industry. In Sweden, the peak concentration occurred around 1970, whereas some other countries, e.g. in eastern and southern Europe, started to reduce their emissions only in the 1980s, or have not yet done so.[216]

In a local perspective, SO_2 concentration in the center of Göteborg has markedly decreased during the last three decades (Fig. 6.2).[217]

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[214] Graedel *et al.*, 1996.

[215] Brimblecombe and Rodhe, 1988; Graedel, 1992.

[216] Mylona, 1993.

[217] Luftföroreningar i Göteborg, 1996.

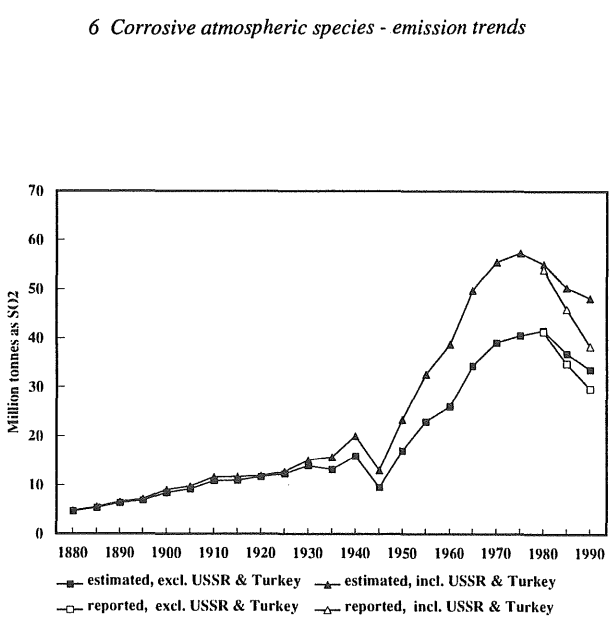

Fig. 6.1 Historical emissions of sulfur dioxide in Europe between 1880 and 1990. Reported totals refer to emissions submitted officially. From Mylona, 1993, p. 22.

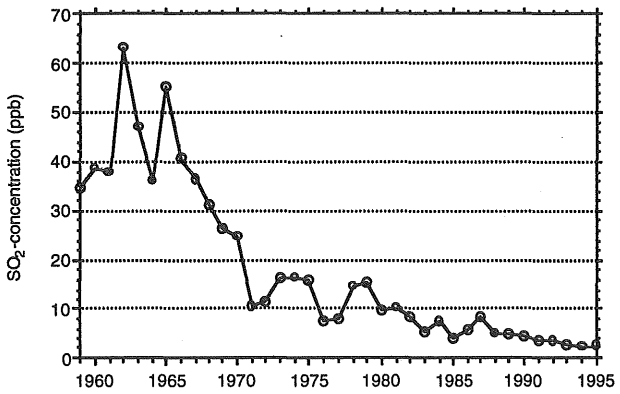

Fig. 6.2 SO_2 concentrations in the center of Göteborg during 1959-95, annual winter half-year averages. It should be noted that the hourly average of SO_2 may be up to 20 times higher than the values indicated in the figure. The figure is based on data from Luftföroreningar i Göteborg, 1996.

6.2.2 NO_x

In a global perspective, anthropogenic and natural emissions of nitrogen oxides (NO_x = NO, NO_2) are roughly comparable. However, anthropogenic emissions contribute to a much greater degree in the industrialized world, and are almost totally related to the combustion of fossil fuels, the main source being transportation.[218] While the concentration of SO_2 in urban air has been slowly decreasing in many parts of the world, NO_x shows a less promising trend.

NO in automotive exhaust oxidizes rapidly to NO_2. Further oxidation of NO_2 yields nitric acid (HNO_3), which is quickly adsorbed by liquid water in clouds or condensates to form aqueous nitric acid.[219]

On a global level, emissions of NO_x began to increase in the late 1800s due to fossil fuel combustion.[220] Historical inventories of nitrogen oxides in the USA exhibited steady emission increases during the last century, and from 1900 to 1980 the increase was about 9 times.[221] In Denmark a gradual increase of NO_x was reported from the 1960s due to the expanded traffic.[222] As the dominating source for NO_x emissions in towns is automotive exhausts, the pollutant levels are clearly related to the intensity of the traffic. In the center of Göteborg, NO_2 and NO_x measurements have been recorded systematically since 1975 (Fig. 6.3).[223]

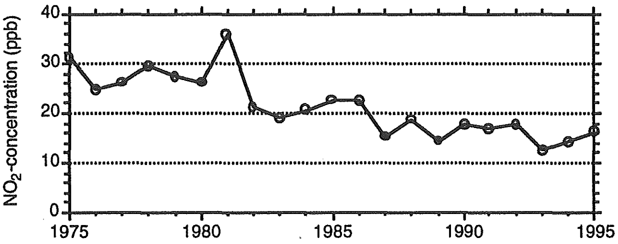

Fig. 6.3 Annual winter half-year averages of NO_2 in the center of Göteborg. The highest measured hourly average of NO_2 may be about 6 times higher than the values displayed. Recorded annual NO_x levels are about twice as high as NO_2 levels. The figure is based on data from Luftföroreningar i Göteborg, 1996.

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[218] Graedel *et al.*, 1996.
[219] Sherwood, 1992.
[220] Galloway, 1996.
[221] Graedel *et al.*, 1996.
[222] Fenger, 1985.
[223] Luftföroreningar i Göteborg, 1996.

6.2.3 O_3

Ozone is one of the most important trace oxidants in the atmosphere and often occurs at higher concentration than SO_2. There has been a significant increase in the ambient O_3 concentration since pre-industrial times and a doubling of tropospheric O_3 is noted in the northern hemisphere. This is mainly due to higher anthropogenic NO_x emissions originating from fossil fuel combustion.[224] In urban atmospheres where high amounts of hydrocarbons and NO_2 occur, irradiation with sunlight leads to the formation of O_3. Thus, photochemical smog may cause very high levels of O_3 in some urban areas during daytime. However, O_3 also tends to be rapidly consumed in urban areas by reaction with NO. Therefore, the O_3 concentrations may be higher and more stable in rural areas, due to the transport of pollutants and lower levels of NO.[225] A negative correlation between O_3 and NO_2 concentrations is accordingly reported from field measurements (Fig. 6.4).[226]

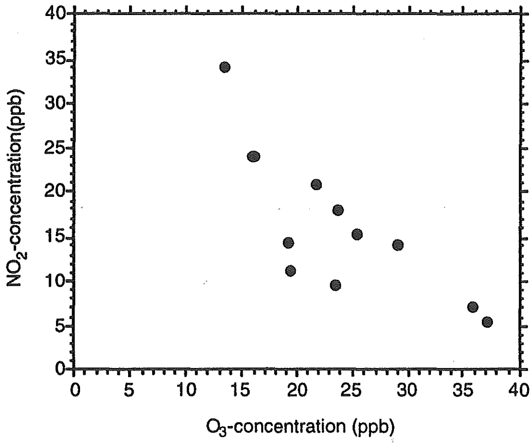

Fig. 6.4 O_3 and NO_2 concentrations (annual averages) at some locations in Göteborg in 1995, showing a negative correlation. The two highest O_3 concentrations indicate measurements in Lerum (suburb) and Botaniska Trädgården (park) respectively, and the lowest O_3 concentration indicates measurements in Gårda (heavy traffic). The highest hourly mean value for Botaniska was 88 ppb. Data from Luftföroreningar i Göteborg, 1996; and Brandberg, 1997, unpubl.

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[224] Crutzen, 1993.

[225] Seinfeld, 1986, p. 37.

[226] Tidblad and Leygraf, 1995; Luftföroreningar i Göteborg, 1996.

6.2.4 NH_3

Atmospheric NH_3 derives primarily from agricultural activities (livestock and fertilizers). NH_3 emissions from increased fertilizer use did not grow significantly until around 1950, at which time they rose rapidly on a global basis and surpassed NO_x emissions in the late 1980s. In the atmosphere, NH_3 neutralizes HNO_3 and H_2SO_4, reducing the acidity in aerosol particles. As a result, particulate ammonium nitrate and ammonium sulfate are common constituents found in atmospheric aerosols and fog. In ecosystems, NH_x deposition has the potential to acidify.[227]

6.2.5 Reduced sulfur gases

Reduced sulfur gases (S(-II) compounds) include hydrogen sulfide (H_2S), carbonyl sulfide (COS), and methyl mercaptan (CH_3SH). They are typically emitted by soils, oceans, swamps, and pulp mills and are generally found in very low concentrations.[228] COS concentrations are rather constant (about 0.6 ppb), while H_2S is variable ranging from 0.003 ppb far away from its source to 3 ppb in the proximity of strong sources.[229]

6.2.6 HCl

HCl is the dominant inorganic gaseous chlorine compound in the atmosphere and an upward trend in concentration has been observed during the last decades.[230] The principal source is reported to be the reaction of acid gases with sea-salt aerosols, e.g. NO_2(g) and NaCl(s) forming HNO_3 and HCl(g).[231] Besides the formation from sea-salt aerosols, HCl is emitted from the combustion of fossil fuel and refuse.[232]

6.3 Particles

Aerosols are defined as relatively stable suspensions of solid or liquid particles in a gas. Atmospheric aerosol particle diameters range between about 0.002 µm and 100 µm, as larger particles (e.g. raindrops ~1 mm; and very fine sand >100 µm) rapidly fall out. Coarse particles (> µm) contain e.g. soil and alkaline material and are typically rich in

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[227] Finlayson-Pitts and Pitts, 1986, p. 547; Galloway, 1996.
[228] Sherwood, 1992.
[229] Graedel, 1992.
[230] Graedel, 1987b.
[231] Eldering *et al.*, 1991.
[232] Graedel, 1987b.

calcium, while fine particles (< μm) contain e.g. elemental carbon, sulfates and ammonium compounds.[233] Typical concentrations in aerosols are depicted in Table 6.2.

Emissions of atmospheric particles arise from a wide variety of human activities, including combustion of fossil fuels, industrial processes, and agricultural practice. Aerosol particles may sorb gases from the atmosphere around them, often incorporating substantial amounts of corrosive species.[234]

Table 6.2 Typical outdoor concentrations of aerosol particles in urban and rural atmospheres. From Sinclair and Weschler, 1986.

	Concentrations of particles (μg/m³)				
Atmosphere	$^{*}SO_4^{2-}$	$^{**}Cl^-$	$^{*}NO_3^-$	$^{*}NH_4^+$	$^{**}Ca^{2+}$
Urban	20	0.3	4	5	2
Rural	4	0.02	2	2	1

* fine particle fraction <2.5 μm
** coarse particle fraction >2.5 μm

6.3.1 Chloride-containing particles

The principal source for chlorine in the atmosphere is sea salt. In marine areas, sea-salt aerosols are formed with an initial composition of sea water (0.4 M NaCl). Particles with a wide range of sizes (0.1 μm to 100 μm) are formed by wave action producing small droplets. The evaporation of water increases the concentration in the droplets and may leave solid particles.[235] Sea-salt aerosols can be far removed from the coast, and may also be scavenged by water and occur in rain, snow, fog and dew.[236] Another source of chloride is the use for de-icing, implying that large amounts of chloride may be found on objects close to roads.[237]

6.3.1 Ammonium sulfate particles

Industrial regions may be dominated by ammonium sulfate in particle fractions originating from NH_3 and SO_2 (Table 6.2). $(NH_4)_2SO_4$ is probably the main constituent of

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[233] Finlayson-Pitts and Pitts, 1986, p. 727.
[234] Graedel, 1992; Lobnig *et al.*, 1993.
[235] Finlayson-Pitts and Pitts, 1986, p. 784.
[236] Graedel, 1987; Livingston, 1991.
[237] Selwyn *et al.*, 1996.

deposited aerosol particles, but mixtures with e.g. $(NH_4)_3H(SO_4)_2$, NH_4HSO_4, H_2SO_4, and NH_4Cl are also possible.[238]

6.3.2 Soot

The major part of soot (= carbon black) particles comes from incomplete fuel combustion. Soot consists mainly of carbon but also contains 10 mol% and more of hydrogen.[239] Soot and SO_2 emissions are correlated in a historical perspective (compare Fig. 6.2 and Fig. 6.5).

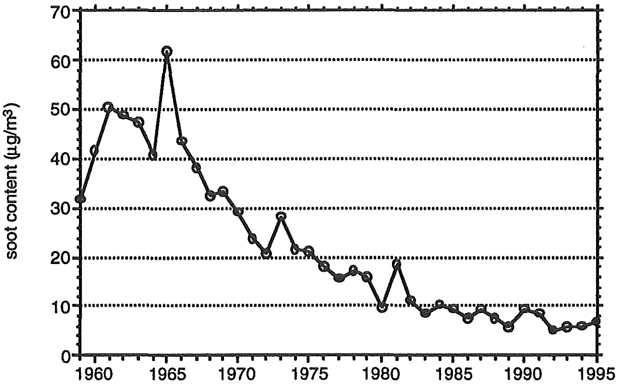

Fig. 6.5 Soot content in the air in Göteborg during 1959-95, annual winter half-year averages (cf. SO_2 in Fig. 6.2). The figure is based on values from Luftföroreningar i Göteborg, 1996.

6.4 Acid deposition

Natural precipitation, rain and snow, is slightly acidic depending on dissolved carbon dioxide in the falling droplets. Therefore, pH in natural rain water is ~5.6. Over the last few decades, rainwater generally has exhibited much greater acidity than the background level, an important contribution coming from the strong mineral acids H_2SO_4 and HNO_3.[240] The pH of cloud and rain water may be calculated using the following simplified formula, which neglects the acidifying contribution from organic acids as well as the neutralization by alkaline soil dust:[241]

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[238] Sinclair and Weschler, 1986.

[239] Bartok and Sarofim, 1991, p. 292.

[240] Wayne, 1985, pp. 200-201; Graedel *et al.*, 1996.

[241] Rodhe *et al.*, 1996.

$H^+ = 2SO_4^{2-} + NO_3^- + HCO_3^- + 2CO_3^{2-} - NH_4^+$

Acid rain is no new phenomenon, but was recognized in the rainwater of the industrial cities of England already in the early part of this century. What is new is the widespread occurrence of acid precipitation.[242] On a global level, fluxes of sulfur and nitrogen to and from the atmosphere are at least ten times larger today than before industrialization.[243] While the global contributions of acidity due to SO_x and NO_x are rather similar today, the proportion attributed to NO_x is predicted to increase in the future.[244]

Scandinavia has been particularly affected by the acid rain problem. Before 1930, there are indications that rain acidity generally exhibited pH>5 outside urban areas. Records kept since the 1950s show that precipitation became increasingly acid until the 1970s, and that the acidity became more widespread geographically (Fig. 6.6).[245] In Sweden, precipitation acidity has shown a quite stable trend during the last two decades. Annual mean pH values for some locations in Göteborg have been measured in the range 3.9-4.9 from 1972 to 1995, the wide range reflecting e.g. the annual amount of precipitation.[246] Thus, the marked decrease of SO_2 emissions (compare with Fig. 6.2) has not affected pH in precipitation significantly.

Fig. 6.6 Increase of precipitation acidity in Scandinavia between 1957 and 1970. The solid lines mark contours of equal pH. From Wayne, 1985, p. 201. Source: Linkens, G., Chem. Engng News 54 (1976) 29.

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[242] Wayne, 1985, pp. 200-201.
[243] Brimblecombe and Rodhe, 1988.
[244] Wayne, 1985, pp. 200-201; Graedel *et al.*, 1996.
[245] Wayne, 1985, pp. 200-201.
[246] Luftföroreningar i Göteborg, 1994; Brandberg, 1997.

Total particulate SO_4^{2-} concentrations (sum of wet and dry deposited S(VI)) seem to have experienced less dramatic changes than SO_2 emissions over the industrial period. In Sweden, SO_4^{2-} concentrations in precipitation have been somewhat reduced (~30%) since the 1970s, while SO_2 concentrations have decreased considerably (Fig. 6.2).[247] Away from the emission sources, particulate SO_4^{2-} concentrations are comparable with those of SO_2, and in areas with very low emissions SO_4^{2-} is significantly higher than SO_2.[248] Concentrations of NO_3^- and Cl^- in precipitation have been relatively constant during the last two decades (Table 6.3).[249]

Table 6.3 Annual concentrations of some ionic species in precipitation in Göteborg during 1972-94 (µM). From Luftföroreningar i Göteborg, 1994.

Concentration (µM)			
SO_4^{2-}	Cl^-	NO_3^-	NH_4^+
40-160	140-370	50-110	60-110

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[247] Mylona, 1993; Hedin *et al.*, 1994.
[248] Mylona, 1993.
[249] Luftföroreningar i Göteborg, 1996.

7 ATMOSPHERIC CORROSION OF COPPER AND BRONZE

The atmospheric corrosion of copper and bronze is primarily due to the abundant supply of moisture and oxygen to outdoor surfaces and to corrosive substances depositing. The corrosion process may have an *electrochemical nature*, thus involving oxidation and reduction reactions, often occurring separately on anodic and cathodic sites respectively. Electrons are transferred in the solid state and ions flow in the electrolyte between the anodic and cathodic sites, corrosion products subsequently precipitating in between these places. Atmospheric corrosion may also have a *chemical nature* which means that transport of electrons is not involved. Such reactions occur e.g. in patina layers of outdoor copper and bronze, and are of great significance for the deterioration of outdoor cultural objects.

The presence of corrosive trace substances such as air-pollutants and particles is decisive for the corrosion behaviour in the atmosphere. Generally, urban atmospheres containing high pollutant levels are more corrosive, causing higher corrosion rates than rural environments. However, for the remarkable metal copper, this correlation does not always exist, and several reports have testified to its complicated corrosion behaviour.

This section describes some crucial factors affecting deterioration processes on outdoor copper and bronze objects, and includes: water; dry deposition of various air-pollutants and particles; formation of cuprite, sparingly soluble or soluble corrosion products; wet deposition; stability and solubility of corrosion products in the patina layer; and the metal composition. The corrosion products are mentioned by their mineral names since they have been described with their formulae in section 5.2; see Table 5.1.

7.1 Influence of water

Atmospheric corrosion is strongly influenced by the presence of water delivered to outdoor surfaces by rain, snow, fog, and humidity in the air. The importance of humidity to corrosion has been reported from the field[250] and from many laboratory

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[250] Forslund and Leygraf, 1997b.

investigations.[251] The relative humidity in outdoor air and the amount of precipitation exhibit wide geographic and yearly variations. As a reference, it could be mentioned that Göteborg had an annual mean value of 77% RH recorded in 1995, the daily mean values ranging between 46 and 97% RH.[252] Annual precipitation is about 600 l/m^2 year in Göteborg.[253]

The presence of water on surfaces enhances the deposition of soluble air-pollutants. The dissolution of gases in the surface water layer may cause secondary aggressive substances to form and leads to increased deposition. The concentration of a gas that may be dissolved is related to the Henry's law coefficients (H_x), e.g. 1.3, $1.3 \cdot 10^{-2}$, $1 \cdot 10^{-2}$ and $1.3 \cdot 10^{-3}$ M/atm for SO_2, O_3, NO_2 and O_2, respectively.[254] An electrolyte may in this way be created on the metal surface, e.g. by:

$$SO_2(g) + H_2O + 1/2O_2 \rightarrow SO_4^{2-} + 2H^+ \qquad [4]$$

This acid surface electrolyte may attack and dissolve the passive film that protects the metal, and an electrochemical corrosion process can start.

At relative humidities below 100% RH, adsorbed water is present on a clean surface and may act as an electrolyte, the number of monolayers reported ranging from 1 to 10 for 25-95% RH.[255] Moreover, water-soluble deliquescent salts deposited on the surface (e.g. NaCl particles), and soluble corrosion products formed during the corrosion process, attract water from surrounding air and form solutions on the surface at certain critical relative humidities that may be crucial for the corrosion rate. Reported critical relative humidities for some salts are e.g.: $CuCl_2 \cdot 2H_2O$, 68%; NaCl, 75%; $(NH_4)_2SO_4$, 80%; $CuSO_4 \cdot 5H_2O$, 97%.[256]

Laboratory investigations showed that copper enters into an active corroding state above 75% RH when very small amounts of SO_2 were present in the air[257] (see Fig. 7.1), or when $(NH_4)_2SO_4$ particles were applied on the surface[258]. When SO_2+O_3 were combined or NaCl particles were applied on the copper surface, the corrosion rate increased considerably already at 70% RH.[259] For some other combinations of air-pollutants, the corrosion process was enhanced at a higher RH, e.g. the SO_2+NO_2 synergism which was active at 90% RH.[260]

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[251] See laboratory investigations reported in the following sections.
[252] Luftföroreningar i Göteborg, 1996.
[253] Luftföroreningar i Göteborg, 1994.
[254] Calvert, 1984 p. 175. According to Henry's law: $[X(aq)] = H_x p_x$.
[255] Phipps and Rice, 1979.
[256] Young, 1967; reported values for 22°C.
[257] **Paper III.**
[258] Lobnig *et al.*, 1993.
[259] **Paper IV and V.**
[260] Eriksson *et al.*, 1993b.

7.2 Dry and wet deposition of corrosive species

One way to classify pollutants is by the medium by which they arrive at the surface.[261]

Dry deposition includes both large particles, aerosol particles and trace gases. Large particles fall according to gravity onto skyward areas, while small particles and trace gases tend to reach all surfaces by turbulent processes and also reach the rain-sheltered surfaces of an object. The flux of pollutants varies on different locations on a statue, and the deposition rate increases where the turbulent transfer is greater, as on the windward side and when the structural shape is complex. There are some critical factors that generally influence the dry deposition rate, such as surface roughness, the presence of surface moisture, and the pollutant concentration in the air. The chemical affinity for the surface also depends on the corrosion products formed.

Wet deposition is defined as pollutants delivered to surfaces by means of precipitation, i.e. rain, snow, and fog. Wet deposition affects all surfaces that are wetted either directly by precipitation or by runoff from other areas. Corrosive substances such as H^+, SO_4^{2-}, Cl^-, and NO_3^- may be dissolved in precipitation (see Table 6.3).

7.3 Deposition of sulfur

Sulfur compounds may be delivered to outdoor copper and bronze surfaces by dry deposition of SO_2 or SO_4^{2-} in aerosols, or by wet deposition of particulate SO_4^{2-} in precipitation. Sulfate may react with the copper and bronze surface and form, e.g. brochantite.

The main supply of sulfur to *rain-sheltered areas* is suggested to occur by *dry deposition of* SO_2, but dry or wet deposition of particulate SO_4^{2-} also occurs. The ratio SO_2/total particulate SO_4^{2-} in the atmosphere has been reported to be one in some urban areas (section 6.4), but deposition velocity[262] is considered to be higher for SO_2 than for aerosol sulfate. Calculations suggest e.g. that the accumulation rate of aerosol particulate SO_4^{2-} may be 0.6 μmol/cm² year in an urban area, and the dry deposition of SO_2 may be 2.5 μmol/cm² year.[263] However, on a surface that has little tendency to absorb SO_2, e.g. on a clean passivating cuprite patina in some conditions or on surface-treated copper,[264] contribution of sulfur by aerosol particulate sulfate is suggested to be more significant.

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[261] This section is based on Sherwood, 1992.

[262] Deposition velocity is defined as the flux of the substance to a surface divided by its concentration in the air, according to Lipfert, 1989.

[263] Calculated for 20 μg SO_4^{2-}/m^3 (see section 6.3) and a deposition velocity of 0.1 cm/s (according to Forslund and Leygraf, 1997a); and for 2 ppb SO_2 (see Fig. 6.2) and a deposition velocity of 1 cm/s (for reactive surfaces according to Johansson, 1990).

[264] **Paper VII**; Appendix 2.

On rain-washed areas, wet deposition of SO_4^{2-} may reach 6 µmol/cm^2 year[265] which is more than what is calculated from dry deposition. However, copper hydroxy sulfates formed on skyward surfaces are probably dissolved due to the acidity in the rain (see section 7.12). Therefore, wet deposition of sulfate is not considered to contribute appreciably to the formation of copper hydroxy sulfates on copper and bronze surfaces. On the other hand, on areas where rain water containing dissolved corrosion products may accumulate, as on horizontal concave surfaces or in depressions, sulfates may again precipitate. A faster greening on such parts of sculptures, e.g. on skyward areas of bases on sculptures, has also been observed.

7.4 Influence of SO_2

SO_2 in the atmosphere is known to accelerate the corrosion of many metals. In the case of copper corrosion, however, the situation is somewhat unclear, as indicated by several investigations in the field.[266] Results from field exposures by Knotkova *et al.* and Kucera *et al.* were interpreted to indicate SO_2 as a decisive factor for corrosion. However, the correlation between dose and response was better for zinc and steel than for copper. In other field exposures by the Swedish Corrosion Institute, the metal loss of copper was shown to be lowest at sites where the corrosion of zinc and steel was highest. Henriksen and Fossestøl carried out field exposures of copper in an environment in Norway containing SO_2 but only minor amounts of other pollutants. Their investigation showed SO_2 to be of minor importance to copper corrosion. The authors considered that the correlation between SO_2 concentration and copper corrosion rates found at other sites was caused by the presence of NO_2. The Norwegian study is supported by Tidblad and Leygraf, who found no correlation between weight increase and SO_2 concentration for copper. In environments with low levels of pollutants a high weight gain was observed and cuprite was identified as the major corrosion product. Stöckle *et al.* also reported surprisingly high initial corrosion rates on copper in rural areas, although decreasing after longer exposure. Further investigations in rural atmosphere by Odnevall and Leygraf showed a rapid cuprite formation on copper during the first days of exposure.

Several laboratory studies under controlled conditions have been performed to address the influence of SO_2 on copper corrosion. Many of these studies[267] involve SO_2 concentrations far in excess of what is found in outdoor atmospheres. Already in the

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[265] Calculated for 600 l/m^2 year and 10^{-4} M SO_4^{2-}, see Table 6.3.

[266] Knotkova *et al.*, 1984; Kucera *et al.*, 1987; Henriksen and Fossestøl, 1989; Tidblad *et al.*, 1991; Stöckle *et al.*, 1993; Rendahl *et al.*, 1995; Tidblad and Leygraf, 1995; Odnevall and Leygraf, 1995.

[267] Vernon, 1931; Sydberger and Vannerberg, 1972; Rozenfeld, 1972; Ericsson and Sydberger, 1977; Chawla and Payer, 1990.

1930s, Vernon investigated the effect of very high concentrations (0.01-10%) of SO_2 on copper and demonstrated the importance of water for the corrosion process. He proposed that SO_2 decreases the local anodic pH sufficiently to cause increased oxide dissolution, and therefore increases the corrosion rate. Exposing copper to humid air containing 10 and 100 ppm SO_2, Ericsson and Sydberger identified sulfite ($(Cu(I)_2Cu(II)(SO_3)_2 \cdot 2H_2O)$) and sulfate ($CuSO_4 \cdot 5H_2O$) as the only crystalline corrosion products formed.

In the last decades, laboratory experiments have been performed with SO_2 in the ppb-range.[268] Abbott first conducted experiments in this low concentration range to show the effects of mixtures of industrial air-pollutants. Rice *et al.* later reported on a correlation between SO_2 concentration and copper corrosion. Strandberg and Johansson, however, performing exposures with a high degree of control, concluded an inverse correlation between SO_2 concentration and copper corrosion, which agrees with the later findings in the field. The presence of cuprite, sulfite and sulfate has been reported on copper exposed to ppb levels of SO_2 in humid air.[269] Strandberg and Johansson found sulfate to be the dominant sulfur species after one day of exposure in such atmospheres.

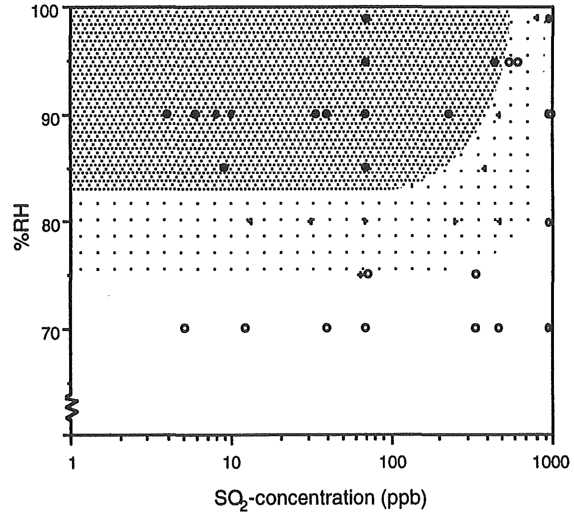

Fig. 7.1 Visual appearance of copper samples after 20 h exposure in atmospheres of various RH and SO_2 concentrations; (●), (+) and (o) indicate black, spotted, and shiny samples, respectively. The shaded fields indicate approximate regions of occurrence for the samples described. From **Paper III**.

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[268] **Paper III**; Abbott, 1974; Rice *et al.*, 1981; Henriksen and Rode, 1986; Eriksson *et al.*, 1993b; Persson and Leygraf, 1990, 1993, 1995; Rickett and Payer, 1995; Song *et al.*, 1995.

[269] **Paper III**; Eriksson *et al.*, 1993b; Persson and Leygraf, 1990, 1993, 1995.

In laboratory studies, little information has been presented concerning the visual appearance[270] of samples. Eriksson *et al.* reported that copper coupons remained shiny after four weeks' exposure in humid air containing 500 ppb SO_2. In a later study by Strandberg and Johansson involving lower levels of SO_2 (69 ppb), a surprising phenomenon appeared. Thus, copper samples developed a dull black cuprite patina (200-300 nm thick) after 20 hours. This dull black appearance formed in humid air (>75% RH) containing 4-69 ppb SO_2, while copper remained shiny at higher SO_2 concentrations or at lower humidity (Fig. 7.1).

The formation of a black or shiny patina is explained by Strandberg and Johansson[271] in terms of an active/passive transition on the copper surface (schematically viewed in Fig. 7.2). It is suggested that the passivating effect of SO_2 at high concentration is caused by the formation of a layer of protective chemisorbed sulfite on the thin invisible air-formed oxide that is assumed to be hydroxylated:

$$\equiv \overset{I}{Cu}\text{-}OH^-(ads) + SO_2(g) \rightarrow \equiv \overset{I}{Cu}\text{-}SO_3H^-(ads) \qquad [5]$$

At low concentrations and high humidity the adsorbed sulfite layer is destroyed due to the formation of soluble species and oxidation to sulfate:

$$\equiv \overset{I}{Cu}\text{-}SO_3H^-(ads) + H_2O + 1/2O_2 \rightarrow \equiv \overset{I}{Cu}\text{-}OH^-(ads) + SO_4^{2-} + 2H^+ \qquad [6]$$

The thin air-formed oxide film is attacked by the acid surface electrolyte and an electrochemical corrosion process can start. Consequently copper is anodically dissolved, oxygen is cathodically reduced, and cuprite is precipitated to form a dull black layer:

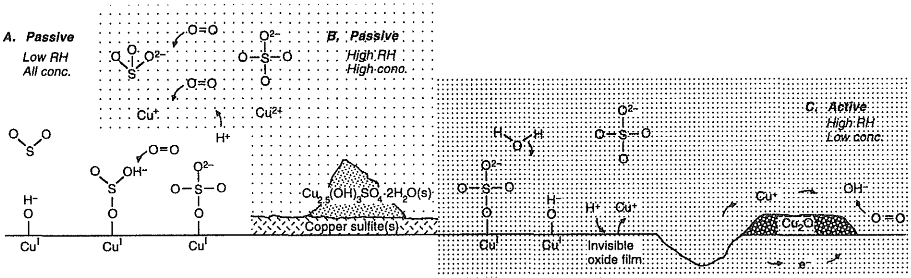

Fig. 7.2 A schematic view of the interaction of SO_2 with a copper surface in humid air. (A) The passive surface at low RH; (A+B) the passive surface at high RH and high concentration; and (A+B+C) the breakdown of the invisible oxide film at high RH and low concentrations, subsequently resulting in active corrosion. From **Paper III**.

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[270] **Paper III** (Strandberg and Johansson, 1997a); Eriksson *et al.*, 1993b.

[271] **Paper III**.

$Cu(s) \rightarrow Cu^+ + e^-$ anodic reaction [7]

$1/4O_2 + 1/2H_2O + e^- \rightarrow OH^-$ cathodic reaction [8]

$Cu^+ + OH^- \rightarrow 1/2Cu_2O(s) + 1/2H_2O$ precipitation of cuprite [9]

Cu^+ may also be oxidized to Cu^{2+} by oxygen, and copper hydroxy sulfates may subsequently precipitate.

It is evident that copper exposed to the outdoor atmosphere can develop a patina similar in appearance, thickness and composition to that found by exposing copper to low levels of SO_2 in the laboratory. In rural areas, copper has been reported to form stains initially and later to turn black, cuprite being the main corrosion product.[272] Some recent field studies have also reported on the high corrosion rates of copper, and the large amounts of cuprite formed at test sites with low levels of pollutants.[273] The laboratory study by Strandberg and Johansson[274] showed that very low levels of SO_2 may transfer copper into an active corroding state forming large amounts of cuprite. An inverse

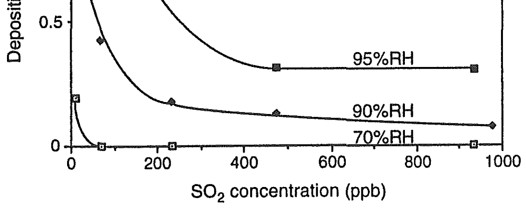

Fig. 7.3 Deposition velocity for SO_2 on copper after 20 h exposure. For an ideal absorber, the deposition velocity is 3.2 mm/s in this experimental setup. The lines are guides to the eye. **Paper III.**

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[272] Holm and Mattsson, 1982; Mattsson and Holm, 1982; Tidblad and Leygraf, 1995; Stöckle *et al.*, 1993; Odnevall and Leygraf, 1995; Rendahl *et al.*, 1995.

[273] Henriksen and Fossestøl, 1989; Stöckle *et al.*, 1993; Odnevall and Leygraf, 1995; Rendahl *et al.*, 1995.

[274] **Paper III.**

correlation between the concentration of SO_2 and the atmospheric corrosion of copper was observed in the absence of other pollutants. The deposition velocity[275] of SO_2 is accordingly very high at low concentrations but sharply decreases with higher concentration (Fig. 7.3), which partly explains the difficulty in finding a clear correlation between SO_2 concentration and copper corrosion in outdoor exposures.[276]

7.5 NO_2 as an oxidant

Eriksson *et al.*[277] showed that NO_2 by itself has a very slight corrosive effect on copper corrosion in humid air (Fig. 7.4). Combining 500 ppb SO_2 and 500 ppb NO_2, the weight gain was strongly increased, however. The synergistic effect resulted when humidity was 90% RH, but not at 70% RH. A synergistic effect in this atmosphere was also shown on bronze alloys by Strandberg *et al.*[278]

Eriksson *et al.*[279] suggested that corrosion is accelerated because of the oxidation of SO_2 by NO_2 on the metal surface to form an acid sulfate electrolyte:

$$SO_2 + 2NO_2 + 2H_2O \rightarrow 2H^+ + SO_4^{2-} + 2HNO_2(g) \qquad [10]$$

The acid electrolyte may attack the air-formed oxide and start an electrochemical corrosion process. High amounts of sulfates were detected after four weeks' exposure and blue-green corrosion products formed on the copper surface. It was also concluded that sparingly soluble copper hydroxy nitrate and soluble nitrite formed. However, extensive amounts of cuprite did not develop (Fig. 7.5). As described above (section 7.4), copper samples turned dull black when exposed at low concentrations of SO_2. The addition of NO_2 to such atmospheres, however, resulted in a shiny sample.[280] These results indicate that the combination of NO_2 and SO_2 slows down cuprite formation. Eriksson *et al.* proposed that NO_2 may be reduced by cuprite on the surface producing $HNO_2(g)$ and nitrite (NO_2^-), and that NO_2 may react in water forming nitrite and nitrate. Strandberg and Johansson[281] suggested that nitrite inhibits copper corrosion, impeding the formation of cuprite.

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[275] See section 7.3.

[276] Knotkova *et al.*, 1984; Kucera *et al.*, 1987; Henriksen and Fossestøl, 1989; Tidblad *et al.*, 1991.

[277] Eriksson *et al.*, 1993b.

[278] **Paper VI.**

[279] Eriksson *et al.*, 1993.

[280] **Paper IV.**

[281] **Paper IV.**

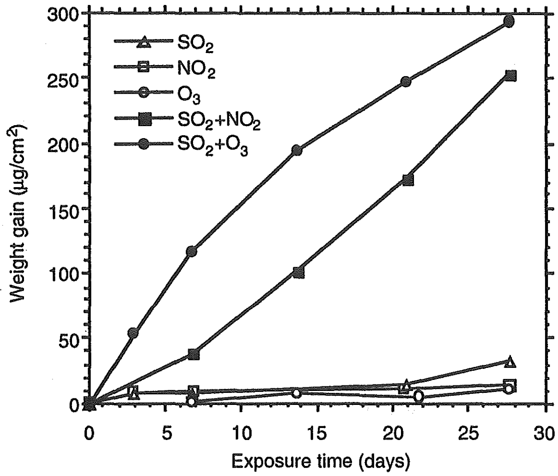

Fig. 7.4 Weight gain of copper samples exposed to SO_2, NO_2, O_3, SO_2+NO_2, or SO_2+O_3 at 90% RH (pollutant concentrations being 500 ppb respectively). Data from **Paper IV**, and Eriksson *et al.*, 1993b.

7.6 O_3 as an oxidant

O_3 concentrations are usually higher outside large cities than in the city centers, as described in section 6.2.3. Recent field studies[282] have shown that the corrosion attack on copper is substantial, both in urban areas rich in SO_2 and NO_x, and in rural areas with low levels of SO_2 and NO_x but higher O_3 levels. Tidblad and Leygraf found the corrosion products to be mainly sulfates and nitrates in areas dominated by SO_2 and NO_2, and cuprite and sulfates in O_3-rich areas.

Tidblad and Leygraf[283] suggested that the corrosion of copper is governed largely by two interactions, SO_2+NO_2 and SO_2+O_3. Zakipour *et al.*[284] studied these interactions in the laboratory at 75% RH, and found that the combination of SO_2+O_3 resulted in a synergistic corrosion effect on copper which was stronger than for SO_2+NO_2. Strandberg and Johansson[285] studied the nature of these interactions and the influence on corrosion product composition in the laboratory, and suggested the influence of the two oxidants, NO_2 and O_3, to be basically different.

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[282] Stöckle *et al.*, 1993; Tidblad and Leygraf, 1995.

[283] Tidblad and Leygraf, 1995.

[284] Zakipour *et al.*, 1995.

[285] **Paper IV**.

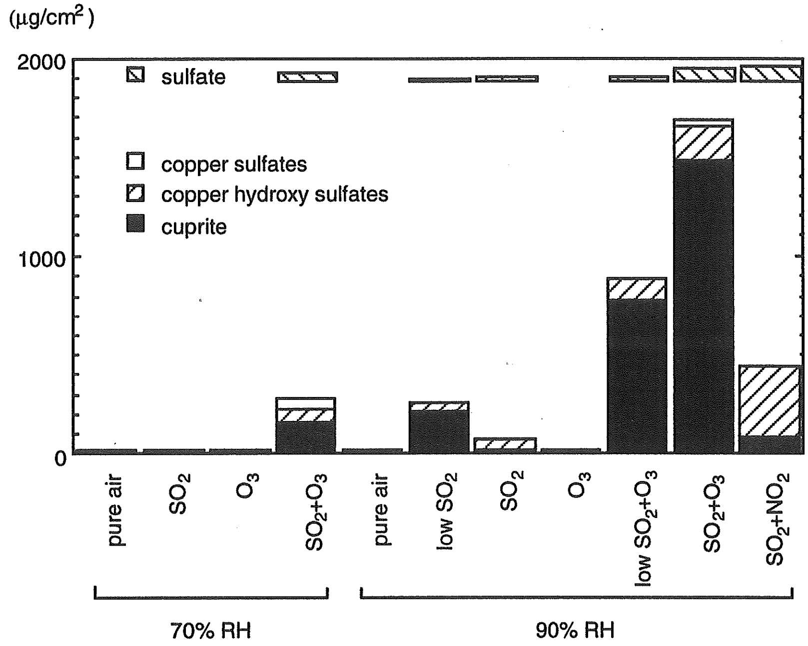

Fig. 7.5 Mass of sulfate, and mass of corrosion products formed on copper after four weeks' exposure in humid air containing different air-pollutants with concentrations: SO_2 = 476 ppb, O_3 = 500 ppb, low SO_2 = 69 ppb, NO_2 = 490 ppb. Illustrated results from **Paper III, IV** and Eriksson *et al.*, 1993b.

Strandberg and Johansson[286] showed that the combination of SO_2 and O_3 resulted in a strong synergistic effect (Fig. 7.4) and the formation of large amounts of cuprite and sulfates (Fig. 7.5). The effect of O_3 was considerable already at 70% RH, whereas NO_2 did not accelerate corrosion at this humidity. At 90% RH the effect of adding O_3 was less marked at low levels of SO_2 than at high SO_2 concentrations which otherwise tended to inhibit copper corrosion.

The authors suggested that O_3 accelerates the corrosion in SO_2-polluted air by increasing the oxidation of adsorbed sulfite:

$$HSO_3^-(ads) + O_3 \rightarrow H^+ + SO_4^{2-} + O_2 \qquad [11]$$

This implies a faster rate of SO_2 deposition (compare reactions [5] and [6]). The increased sulfate formation creates an acid electrolyte on the surface leading to the dissolution of the protective air-formed oxide film. An electrochemical corrosion process can start, according to reactions [7], [8] and [9] where copper is anodically dissolved,

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[286] **Paper IV.**

oxygen is cathodically reduced and cuprite is precipitated forming a dull black layer. The main cathodic process is suggested to be oxygen reduction, even if O_3 also is assumed to take part as a cathodic depolarizer.

In the laboratory study by Strandberg and Johansson,[287] the presence of various copper sulfates (see Table 5.1) was suggested to be related to pH on the surface. Soluble copper sulfate and $Cu_{2.5}(OH)_3SO_4 \cdot 2H_2O$ were identified in the more acid environments created when large amounts of sulfates formed, e.g. when SO_2 and O_3 were combined, while brochantite formation was favoured when smaller amounts of sulfates were formed, e.g. at 69 ppb SO_2 (Fig. 7.5).

7.7 Influence of other gaseous air-pollutants

7.7.1 *H_2S and COS*

Copper and bronze are susceptible to reduced sulfur gases and the corrosion products may be the black copper sulfides, e.g. chalcocite (Cu_2S) and covellite (CuS). The low atmospheric concentrations and low solubility suggest these trace gases to be of minor importance in outdoor conditions. Accordingly, sulfides are only rarely identified in copper patinas.[288] On the other hand, it may be noted that artificial patination of sculptures with various sulfides has been, and is still, a common practice and may result in the formation of sulfides. However, black areas on outdoor objects have sometimes, albeit without analytical support, been assigned to sulfides.

7.7.2 *HCl*

A few laboratory studies deal with the effect of hydrogen chloride on the atmospheric corrosion of copper.[289] Working with very high pollutant concentrations (%-levels), Vernon concluded that HCl was more deleterious than SO_2 towards copper at 50% RH. Feitknecht reported that at low HCl pressure (46 ppb) a thin protective film of cuprite slowly built up on copper, and that nantokite (CuCl) later appeared while chloride accumulated on the surface. The corrosion rate was reported to slow down, reaching a steady state after some months' exposure. At higher HCl pressure (1.8 ppm), loosely attached copper hydroxy chloride formed besides cuprite and nantokite, and the corrosion rate remained nearly constant.

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[287] **Paper IV.**

[288] Graedel, 1987a.

[289] Vernon, 1931; von Feitknecht, 1952; Feitknecht, 1959.

7.8 Influence of corrosive particles

The size and shape of particles, and their chemical composition, determine their deposition and interaction with the corrosion processes. Hygroscopic particles can create an electrolyte on a metal surface and enhance corrosion, whereas alkaline materials from e.g. soil and dust may serve as buffers.[290]

7.8.1 Sodium chloride

In marine atmospheres, where sea-salt aerosols are abundant, copper turns brownish during the first year of exposure, while signs of green patina may be observed after six to seven years.[291] Salt particles may accumulate in rain-sheltered areas that often contain copper hydroxy chlorides in combination with copper hydroxy sulfates and cuprite.[292] Dry deposition rates of chloride on outdoor surfaces in coastal areas have been reported in the range 0.6-3 µmol/cm² year,[293] but a thousand times higher deposition rates may occur close to the seashore.[294]

Feitknecht and Schütz[295] investigated some metals in chloride solutions in the laboratory, and proposed mechanisms for the formation of corrosion products. Eriksson *et al.*[296] reported that the addition of small amounts of sodium chloride caused a marked increase in the corrosion rate of bronze in humid air.

Strandberg and Johansson[297] found that the corrosive effect of applying NaCl to copper was very strong in pure air, or in air containing O_3 or SO_2 (compare Figs. 7.5 and 7.6). Large amounts of cuprite, red in colour, formed when samples were exposed at 70 and 90% RH. The corrosion rate was correlated to the amount of chloride added on the surface and to humidity. The amount of NaCl applied (calculated to be 0.4-8.8 µmol/cm² year) corresponded well to the dry deposition rates reported from the field (see above).

Corrosion in pure air

Strandberg and Johansson[298] reported that in the case of pure humid air the corrosion rate increased considerably for small amounts of NaCl added, but tended to saturate at higher levels of chloride. Large amounts of cuprite and tenorite formed, and nantokite,

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[290] Graedel, 1992.
[291] Holm and Mattsson, 1982.
[292] **Paper II**; Selwyn *et al.*, 1996.
[293] Graedel, 1987b; Livingston, 1991.
[294] Kucera *et al.*, 1987.
[295] Feitknecht and Schütz, 1955.
[296] Eriksson *et al.*, 1993a.
[297] **Paper V**.
[298] **Paper V**.

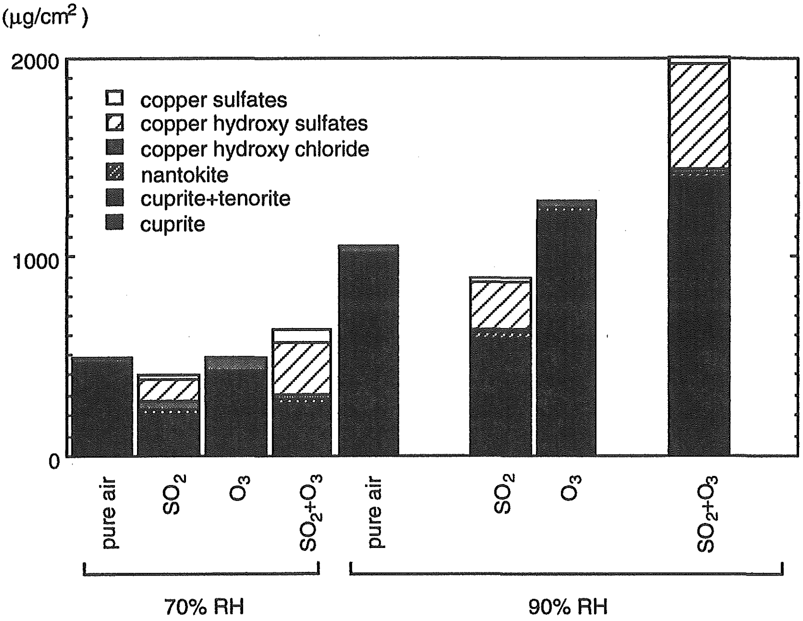

Fig. 7.6 Mass of corrosion products formed on copper pretreated with NaCl after four weeks' exposure in humid air containing different air-pollutants with concentrations: $SO_2 = 476$ ppb, $O_3 = 500$ ppb. Illustrated results from **Paper** V extrapolated for 20 µg NaCl/cm² (corresponding to 4.5 µmol/cm² year). This figure should be compared with Fig. 7.5 presenting results without NaCl.

clinoatacamite and malachite ($Cu_2(OH)_2CO_3$) were also identified. The authors suggest that NaCl increases the surface conductivity on copper at 70% RH, and that an electrochemical corrosion process is initiated by the break-down of the passive film due to the formation of soluble copper(I) complexes:

$$1/2Cu_2O(\text{air-formed oxide}) + 2Cl^- + H^+ \rightarrow CuCl_2^- + 1/2H_2O \qquad [12]$$

Cu^+ ions produced in the anodic dissolution (reaction [7]) may precipitate as nantokite, by migration of chlorides to the *anodic sites*:

$$Cu^+ + Cl^- \rightarrow CuCl(s) \qquad [13]$$

In the presence of moisture and air, nantokite is suggested to be oxidized to form copper hydroxy chlorides:

$$3CuCl(s) + 3/4O_2 + 3/2H_2O \rightarrow Cu_2(OH)_3Cl(s) + Cu^{2+} + 2Cl^- \qquad [14]$$

Copper(II) chloride ($CuCl_2 \cdot xH_2O$) is more deliquescent than NaCl and forms an aqueous solution at humidities above 68%.[299] The presence of copper(II) chloride may therefore contribute to the formation of an aqueous electrolyte, and this becomes especially important at e.g. 70% RH.

The oxidation of CuCl(s) close to the anodic sites implies a local pH decrease due to the acidity of the $Cu(H_2O)_4^{2+}$ ion, and a high chloride activity. This may further help to break down the passive layer to enhance anodic dissolution. Nantokite is reported to be stable in acid conditions, if water and oxygen are not present.[300] Accordingly, it has been observed under the cuprite layer in pockets close to the metal on archaeological objects.[301]

Reduction of O_2 occurs at the *cathodic areas* and cuprite subsequently precipitates (reactions [8] and [9]).

The formation of nantokite and hydroxy chlorides implies a net release of hydroxide ions on the copper surface, which results in a pH increase on the cathodic regions:

$$2Cu(s) + O_2 + 2H_2O + Cl^- \rightarrow Cu_2(OH)_3Cl(s) + OH^- \qquad [15]$$

The activity of carbonate in the basic surface electrolyte may thus become much higher, which explains the presence of malachite.

Corrosion in air containing SO_2

Strandberg and Johansson[302] showed in their laboratory study that the presence of SO_2 slowed down the corrosion rate on copper treated with NaCl. Cuprite was abundant on the samples, while tenorite was absent due to the fast reaction with SO_2 which also explains why tenorite is rarely found in outdoor conditions. Nantokite, clinoatacamite and brochantite additionally formed in this environment. There are indications that NaCl favours formation of copper hydroxy sulfates exhibiting lower SO_4^{2-}/OH^- ratios than without NaCl, due to the increased pH on the surface according to reaction [15].

Corrosion in air containing SO_2 and O_3

In air containing a combination of SO_2 and O_3 at 90% RH, corrosion was rapid without NaCl. The addition of small amounts of salt to the copper surface (chloride deposition typical for inland areas) in this environment was surprisingly shown to result in a marked decrease of the corrosion rate.[303] A minimum occurred for a deposited amount corresponding to 0.7 $\mu mol/cm^2$ year, while approximately the same corrosion rate as without NaCl (compare Figs. 7.5 and 7.6) was reached for 4.5 $\mu mol/cm^2$ year (typical

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[299] Young, 1967.
[300] Feitknecht, 1959.
[301] Scott, 1990.
[302] **Paper V.**
[303] **Paper V.**

for marine environment). The presence of NaCl also favoured the formation of antlerite, which was not detected in the absence of NaCl. Accordingly, antlerite is found together with copper hydroxy chlorides on outdoor copper and bronze.

7.8.2 Ammonium sulfate particles

Lobnig *et al.*[304] investigated the effect of $(NH_4)_2SO_4$ deposited on copper. Above 75% RH they found a localized attack with the formation of cuprite, and of brochantite or antlerite. Thus, the formation of antlerite was favoured in the presence of heavy ammonium sulfate deposition, which was also shown to be the case when NaCl was present on a copper surface (see above).[305] Lobnig *et al.* suggested that ammonium reacts to ammonia that eventually evaporates from the surface, while sulfate forms corrosion products with copper.

7.8.3 Soot particles

Laboratory studies in humid air showed that active carbon mixed with cuprite powder enhanced the oxidation of sulfite remarkably in SO_2+NO_2 atmosphere.[306] This indicates that carbon deposits on a cuprite patina may increase the sulfation. Carbonaceous particles are also believed to catalyze the oxidation of SO_2 on calcareous stone, and a high degree of sulfation has been noted in black crusts on monumental stone.[307]

7.9 Cuprite and cupric salt formation in the atmospheric corrosion

The types of corrosion products formed are of great importance for the visual appearance, the subsequent corrosion behaviour and the dissolution of corrosion products by rain, etc. Thus, the formation of large amounts of *dark cuprite* early during exposure, resulting in a high metal loss, may in a longer perspective lead to a lower corrosion rate. On the other hand, a corrosion process forming mainly sparingly soluble or soluble *green copper salts* may produce a patina with poorer protective properties due to dissolution and washing-out of the compounds, or due to deliquescent salts that may create an electrolyte on the surface.

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[304] Lobnig *et al.*, 1993.

[305] **Paper V.**

[306] **Paper VII.**

[307] Fassina, 1988.

The laboratory studies by Strandberg and Johansson[308] demonstrate that the corrosion rate and the corrosion product composition depend critically on the combination of pollutants. Thus, the results displayed in Figs. 7.5 and 7.6 show that considerable amounts of *cuprite* form in certain humid environments. This was the case when SO_2 concentration was low, when SO_2 and O_3 were combined, or when NaCl was deposited on the copper surface. In all these atmospheres the cuprite formation was larger than the formation of cupric salts, and the weight increase of samples slowed down during the course of the four-week exposures (see e.g. Fig. 7.4). When SO_2 and NO_2 were combined, however, the cuprite formation was smaller whereas the formation of *cupric salts* was greater and the weight gain curve did not slow down. The formation of *soluble copper sulfate* was considerable when deposition of SO_2 was fast, e.g. when SO_2 and O_3 were combined. This is connected with the acid environment created by the oxidation of SO_2 (reaction [11]), which implies that copper sulfate becomes a stable phase (see Fig. 7.7). Deliquescent $CuCl_2{\cdot}xH_2O$ was suggested to form in the presence of NaCl, which may contribute to the formation of an acidic aqueous electrolyte increasing the corrosion.[309]

Accordingly, recent field studies show an initially large formation of *cuprite* in *rural areas* (low SO_2+O_3), whereas *cupric compounds* seem to be more predominant in *urban areas* (high SO_2+NO_2).[310] The corrosion rate is also reported to be very high initially at sites with high RH and low SO_2 but soon levels off, while the corrosion rate is more linear at exposure sites with high levels of SO_2 and probably high NO_2 levels as well.[311]

This dissertation suggests that the changed pollution situation during the last decades, e.g. with strongly reduced SO_2 emissions (see section 6.2.1), has increased the *formation ratio cuprite/cupric salt* in many locations. The statement that copper roofs and sculptures in low-polluted areas only tarnish brown, and turn green much more slowly nowadays than previously, also supports this hypothesis.

Efforts to correlate the atmospheric corrosion of copper with environmental parameters such as the concentration of SO_2, etc., have generally been unsuccessful.[312] This is connected with the complex chemistry and corrosion behaviour of copper, as revealed above.[313] If only corrosion rates of samples are reported, while description of the corrosion process and composition of corrosion products is lacking, it is clear that field exposure studies will come short of finding any correlation. The formation of different corrosion products is also crucial for the visual appearance of cultural objects. Thus, it is suggested that future field and laboratory investigations try to distinguish

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[308] **Paper, III-V.**

[309] Young, 1967.

[310] Stöckle *et al.*, 1993; Tidblad and Leygraf, 1995.

[311] Stöckle *et al.*, 1993; 1996.

[312] Knotkova *et al.*, 1984; Henriksen and Fossestøl, 1989; Tidblad *et al.*, 1991.

[313] **Paper III-V.**

between cuprite-forming corrosion and corrosion resulting in the formation of cupric salts, based on the relative amount of corrosion products formed. The correlation with environmental parameters may also be more successful in this way.

7.10 Thermodynamic stability of copper patina compounds

The concentrations of air-pollutants and the chemistry of precipitation have changed markedly during the last century due to anthropogenic activity, and as a result, alterations in the appearance of old outdoor objects have been observed.[314] Nassau *et al.*[315] considered that the change in rain composition is unlikely to have any significant effect on the thermodynamic stability of compounds in copper patinas. However, they suggested that fog, being more acid, has the potential to produce substantial material degradation. Livingston[316] also claimed that the acid rain has no effect on the mineralogy of the patina on the statue of Liberty in New York. However, he calculated that sea-salt deposition nowadays promotes the formation of copper hydroxy chlorides in sheltered areas, whereas previously, a uniformly green copper hydroxy sulfate patina formed on these areas due to higher SO_2 levels.

Regions of relative stability for some frequently occurring copper patina compounds in equilibrium are shown in Fig. 7.7. The figure indicates that brochantite, antlerite, and chalcantite are stable in regions of successively increasing acidity and sulfate ion concentration. The phase favoured when SO_2 is deposited on a surface depends partly on pH and sulfate ion concentration in the electrolyte. All the sulfates displayed below have been identified during laboratory studies; moreover they have been found in rain-sheltered areas on outdoor copper and bronze, where the predominant supply of sulfur to the surface is suggested to be by dry deposition of SO_2.

In horizontal and inclined parts of outdoor copper or bronze objects, where precipitation is heavy, *brochantite* is calculated to be the stable patina compound (as at the X in Fig. 7.7), which is also consistent with results from the field. Brochantite is stable in relation to antlerite at typical precipitation concentrations when $pH>3.4$, and antlerite is stable in relation to soluble chalcantite when $pH>2.2$.

Antlerite is stable in a lower pH range than brochantite and has been proposed to be the preferred crystalline form in the case of fog, where acidity and sulfate concentration may be high.[317] It has been suggested that the rain in previous times contained higher

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[314] **Paper II**; Perocco, 1979; Livingston, 1991.

[315] Nassau *et al.*, 1987b.

[316] Livingston, 1991.

[317] Graedel, 1987a.

levels of acidity and that this favoured the growth of antlerite.[318] However, there is no indication that recently inaugurated sculptures in the first part of this century exhibited this compound.[319] The formation of this hydroxy sulfate is probably connected with kinetic factors (section 7.11.1).

It should be mentioned that the hydroxy sulfates $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$ and *posnjakite*, not displayed in the stability diagram, are probably metastable compounds.[320]

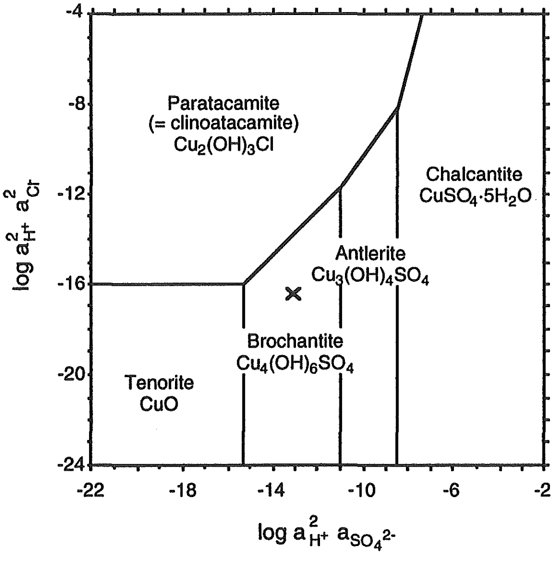

Fig. 7.7 Relative stabilities of copper patina compounds calculated for tenorite, $pK_s= 20.4$; brochantite, $pK_s= 68.8$; antlerite, $pK_s= 47.2$; and clinoatacamite, $pK_s= 34.5$. Data from Sillén and Martell, 1964. The stability of chalcantite was computed by Woods and Garrels, 1986, using free energy of formation values. Typical ion concentrations and pH in rain in Göteborg (pH=4.5; 80 µM SO_4^{2-}; 200 µM Cl^-) are indicated with a cross.

Copper hydroxy chlorides were calculated to be thermodynamically stable at chloride concentrations present in sea water (0.4 M), and were suggested to be stable near the top range of salt concentrations found in rain water and fog (4 mM).[321] However, chloride concentrations may increase on the surface by evaporation and accumulation, explaining the frequent occurrence of hydroxy chlorides in rain-sheltered areas on copper and

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[318] Graedel and Franey, 1986.

[319] Vernon, 1932; Livingston, 1991.

[320] **Paper VII**; Nassau *et al.*, 1987b.

[321] See Fig. 7.7; Graedel, 1987a; Livingston, 1991.

bronze. Three well-defined polymorphs, atacamite, botallackite and clinoatacamite (=paratacamite, see section 5.2), are reported, all being known as minerals.[322] Botallakite is less stable than the other two and is reported to occur only in slightly acidic environments.[323] The relative stabilities of atacamite and paratacamite (=clinoatacamite) and conditions governing the formation of the dimorphs have been widely discussed, but no general agreement has been reached.[324] The dimorphs have similar thermodynamic stability, and formation of the phases probably depends on kinetic factors.[325] Paratacamite (=clinoatacamite) has been proposed to be the stable phase at ambient temperatures.[326]

Tenorite is indicated (Fig. 7.7) to be stable only at high pH and very low chloride and sulfate ion activity.

The stability of *malachite* in outdoor conditions has been discussed in the literature.[327] Lewin reported malachite to be stable at normal atmospheric CO_2 pressure (i.e. ≈350 ppm). In contrast, Graedel claimed that the concentration of CO_2 in air is too low for malachite to be stable. One of the arguments was that this corrosion product has not been unambiguously observed on copper in outdoor environments. Thermodynamic calculations by Woods and Garrels indicate that malachite is more stable than paratacamite (=clinoatacamite) at high pH in equilibrium with air. In agreement with this, Strandberg and Johansson[328] found malachite on NaCl-treated copper that developed a high pH on the surface when exposed in pure humid air (reaction [15]). Thus, malachite may indeed form on copper exposed to pure humid air when salt is deposited on the surface. The reason for not finding this corrosion product in the atmosphere is suggested to be due to the presence of other species, e.g. SO_2.

7.11 Reactions of copper patina compounds in the atmosphere

Aged copper and bronze objects in outdoor environments exhibit several constituents in the patina layer with different properties, e.g. of colour and ability to protect the metal surface, to react with species in the atmosphere, and to be dissolved by the rain. Air-pollutants depositing on copper and bronze patina may cause reactions to occur, and may convert patina compounds to new phases which may result in new characteristics of the patina.

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[322] Jambor *et al.*, 1996.
[323] Feitknecht, 1959.
[324] Sharkey and Lewin, 1971; Woods and Garrels, 1986; Scott, 1990; Pollard *et al.*, 1992a.
[325] Woods and Garrels, 1986.
[326] Pollard *et al.*, 1992a.
[327] Lewin, 1970; Woods and Garrels, 1986; Graedel, 1987a.
[328] **Paper V.**

7.11.1 Influence of some air-pollutants on patina compounds

Copper oxides

Strandberg[329] investigated reactions occurring on pure patina compounds in synthetic atmospheres containing ppb-levels of air-pollutants. The results showed that cuprite and tenorite were reactive to SO_2 in humid air. Tenorite acted as an ideal absorber for SO_2, rapidly forming brochantite and $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$. The reaction of cuprite with SO_2 was slight, however, corresponding to the formation of a chemisorbed sulfite layer on the surface. When O_3 was added to the SO_2-containing air, oxidation of adsorbed sulfite was rapid on cuprite, and $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$, antlerite, and brochantite formed. NO_2 was not an active oxidant in the sulfation of cuprite in humid air. The results are in agreement with the abundant occurrence of cuprite close to the metal surface in outdoor environments, but also demonstrate that an exposed cuprite patina may be converted to hydroxy sulfates in the presence of SO_2 and a strong oxidant such as O_3.

Copper hydroxy sulfates

In the laboratory study by Strandberg,[330] brochantite and antlerite did not react in SO_2-environments, even when O_3 or NO_2 was present. This stability is consistent with the frequent occurrence of brochantite and antlerite in outdoor patina. Brochantite has previously been reported to be stable under a wide variety of chemical conditions,[331] and is also the most common copper hydroxy sulfate in nature.[332]

The hydroxy sulfate $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$, however, converted to antlerite in humid SO_2-containing atmospheres, and it is proposed to be a metastable precursor in both the brochantite and antlerite formation.[333] This property explain its scarcity in outdoor environments and this compound is therefore suggested to indicate recent active corrosion.

Wheather brochantite or antlerite is formed from $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$ is suggested to be determined by e.g. the pH of the surface (Fig. 7.7). In the laboratory studies by Strandberg,[334] antlerite was found on cuprite or on NaCl-pretreated copper, after four weeks' exposure in atmospheres containing the combination of SO_2 and O_3. In these cases high amounts of SO_2 were deposited, implying increased acidity, which may partly explain the presence of antlerite. Another crucial factor for antlerite formation is suggested to be the relatively unfavourable kinetics of formation. Pollard *et al.*[335] reported that antlerite did not crystallize from solution below 35°C, and that it occurs rarely as a natural mineral in temperate regions. At ambient temperature, the authors

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[329] **Paper VII.**
[330] **Paper VII.**
[331] Nassau *et al.*, 1987b.
[332] Woods and Garrels, 1986.
[333] **Paper VII.**
[334] **Paper VII and V.**
[335] Pollard *et al.*, 1992.

proposed that the formation of antlerite occurred via another copper hydroxy sulfate, which Strandberg and Johansson[336] concluded to be $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$. In agreement with this, antlerite is mainly found outdoors in sheltered areas on sculptures that have been exposed in the outdoor environment for several decades (see section 5.2).

It has been suggested that the acid rain may attack brochantite, converting it to the slightly more soluble antlerite.[337] However, no evidence for such conversion in acid solution has been provided.[338] The laboratory exposures by Strandberg[339] mentioned above also indicate the stability of both these phases. Antlerite is uncommon in rain-washed areas, however. The reason for this scarcity is suggested to be due to its slow kinetics of formation. Preliminary experiments indicate $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$ to be slightly more soluble than the other hydroxy sulfates,[340] which suggests that this precursor thus may be washed out by the rain before antlerite formation is obtained.

Copper hydroxy chlorides

The laboratory study by Strandberg[341] showed that copper hydroxy chlorides formed soluble copper sulfate ($CuSO_4{\cdot}xH_2O$) when exposed to SO_2 (reaction [16]). The mixture of antlerite and hydroxy chlorides, which often is present in rain-sheltered areas, also resulted in the formation of the soluble copper sulfate in this environment.[342] An acid environment is created due to the oxidation of SO_2 which produces hydrogen ions, explaining the stability of soluble copper sulfate (see Fig. 7.7). Accordingly, chalcantite has been identified in sheltered areas on outdoor sculptures. The laboratory study[343] also indicated a deliquescent copper salt, probably being soluble copper chloride ($CuCl_2{\cdot}xH_2O$) forming on the copper hydroxy chlorides in SO_2 environment, and the following reaction is suggested:

$$Cu_2(OH)_3Cl + 3/2SO_2 + 3/4O_2 \rightarrow 2Cu^{2+} + Cl^- + 3/2SO_4^{2-} + 3/2H_2O \qquad [16]$$

The release of soluble copper chloride may create an acid aqueous electrolyte, which may cause severe corrosion on outdoor copper and bronze objects. Thus, the reaction of copper hydroxy chloride, abundant in rain-sheltered areas on outdoor copper and bronze, with SO_2-containing air may result in pitting corrosion. Indications of severe pitting in rain-sheltered areas have been observed on old monuments.[344]

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[336] **Paper VII.**

[337] Nielsen, 1984.

[338] Nassau *et al.*, 1987b.

[339] **Paper VII.**

[340] Appendix 1.

[341] **Paper VII.**

[342] **Paper VIII.**

[343] **Paper VII**

[344] Strandberg and Rosvall, 1994; and an observation from a 19th-century monument in central London during conservation.

7.11.2 *Influence of sodium chloride on patina compounds*

Laboratory results by Strandberg[345] showed that *cuprite* treated with NaCl, and exposed in humid air, formed copper hydroxy chlorides:

$$Cu_2O + Cl^- + 2H_2O + 1/2O_2 \rightarrow Cu_2(OH)_3Cl + OH^- \qquad [17]$$

This demonstrates that the thin cuprite patina, present on copper and bronze objects recently placed outdoors, may be converted to hydroxy chlorides by sea-salt deposition on the surface. In agreement with this, copper hydroxy chloride was detected on a bronze sculpture as the first crystalline phase appearing besides cuprite in a marine environment.[346] This hydroxy chloride patina probably is less protective than a pure cuprite patina.

Reaction [17] implies a pH increase on the surface, due to the reduction of oxygen producing hydroxide ions. When O_3 was added to the air, *tenorite* formed as well, which indicates a faster oxidation occurring. Moreover, pure tenorite did not react with NaCl in humid air. Thus, tenorite, being thermodynamically stable at high pH, may become stable in a chloride-containing environment (see Fig. 7.7). Hypothetically, this indicates that tenorite may be a stable phase on copper alloys in "clean" marine environments. However, since minute amounts of SO_2 often are present even in unpolluted air, tenorite may react rapidly and form copper hydroxy sulfates.[347]

The laboratory study by Strandberg[348] showed that salt addition on *cuprite* resulted in an increased sulfation when SO_2 was added to the humid air. In fact, the NaCl-treated cuprite acted as an ideal absorber for SO_2, forming hydroxy sulfates besides hydroxy chlorides. The increased sulfation is suggested to be caused by the increased basicity on the surface. This agrees with the findings of hydroxy chlorides and hydroxy sulfates occurring together, reported from the field. The laboratory study shows that cuprite with NaCl applied is converted to atacamite, clinoatacamite, brochantite, and $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$ in an atmosphere containing SO_2. The same set of corrosion products was found on a dark smooth area on a sculpture in an outdoor environment.[349] In the laboratory an additional, unknown phase (phase II) was identified on copper oxides in the environment with salt and SO_2. This corrosion product is tentatively suggested to be a copper hydroxy chloride sulfate.

On the basis of thermodynamic calculations, it has previously been suggested that hydroxy chloride formation is favoured only in areas sheltered from rain water, and that

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[345] **Paper VIII.**
[346] **Paper II.**
[347] **Paper VII.**
[348] **Paper VIII.**
[349] **Paper II.**

brochantite formation is favoured where rain water hits the surface.[350] It has also been claimed that rain has no effect on the stability of the patina.[351] Strandberg[352] showed a remarkably fast reaction occurring on *antlerite and brochantite* when salt solution was added, resulting in quantitative formation of copper hydroxy chloride. This demonstrates that copper hydroxy chlorides may indeed form on all parts of an outdoor sculpture, including rain-exposed areas containing brochantite, when sea salt is deposited on the surface. The lack of occurrence of these compounds in areas heavily exposed to the rain is suggested to be due to conversion of the copper hydroxy chlorides to soluble copper sulfates and copper chlorides by dry deposition of SO_2 as described above (reaction [18]). Thus, a progressing cyclic weathering may occur on brochantite patina in rain-exposed areas that may be severely deteriorating, including the formation of hydroxy chlorides by sea-salt deposition or precipitation, the conversion to soluble copper sulfate and chloride by dry deposition of SO_2, and subsequently the dissolution and washing-out of the soluble corrosion products by the rain:

$$Cu_4(OH)_6SO_4 \xrightarrow{Cl^-} Cu_2(OH)_3Cl + SO_4^{2-} \xrightarrow{SO_2} CuSO_4 + Cl^- \quad [18]$$

7.12 Dissolution of patina compounds

The release of heavy metals from constructions to the biosphere has been recognized as a problem, since increased concentrations of metals in soil and water may be harmful in a long perspective.[353] The amount of copper in waste-water sludge originating from the atmospheric corrosion in Göteborg has been estimated to be a minor part, the main source being the corrosion in water piping systems.[354] The green discoloration on adjacent stone bases of sculptures shows that the atmospheric corrosion of copper and bronze contributes to the release of metal ions. This obvious dissolution of copper compounds plays an important role in the degradation of outdoor objects, but is probably of minor importance for the biosphere.

In a field study in Stockholm,[355] the amount of *copper in runoff* from exposed copper coupons was found to be *stable with time* (2.1 μmol/cm^2 year), while the corrosion rate was highly time-dependent. The ratio between copper in runoff and the mass loss of copper was low in the beginning (7% after a month) but increased with

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[350] Livingston, 1991.
[351] Nassau *et al.*, 1987b; Livingston, 1991.
[352] **Paper VIII.**
[353] Persson and Kucera, 1996.
[354] Elfström-Broo, 1997, unpubl.
[355] Odnevall-Wallinder and Leygraf, 1997.

time, probably to approach 100% after many years of exposure. The stable runoff rate was explained to be connected with the high initial cuprite formation and dissolution.

This thesis suggests that copper in the runoff mainly *originates from cupric salts*, forming e.g. by dry deposition of SO_2, which is subsequently washed out by the rain. Estimations based on equilibrium calculations[356] show that dissolution of cuprite is considerably less than dissolution of copper hydroxy compounds. Considering that more soluble cupric salts may form as well in some environments, e.g. with high SO_2 deposition, these compounds may contribute to the runoff as well.

A *higher dissolution rate* of copper has been observed in the field with *increasing pollution*.[357] This may indicate that more cupric salts may form at higher pollutant levels, and agrees with the results from the laboratory.[358] A higher cuprite/cupric salt ratio was thus found at exposure conditions which may be representative for low-polluted atmospheres, e.g. low SO_2+O_3, than at conditions representing polluted air, e.g. high SO_2 or high SO_2+NO_2 (Fig. 7.5).

Comparing two investigations from the 1950-60s and the 1990s,[359] the corrosion rate and the retained amount of corrosion products in rural areas were only slightly higher in the early investigation. There is some indication, however, that the fraction adhering was higher in the 1950-60s. In Stockholm, the corrosion rate has decreased since the 1950-60s (6.9 mg/cm^2 per 7 years, 1965; and 2.1 mg/cm^2 per 8 years, 1995), but the ratio of adhering corrosion products/corroded copper has been constant. Persson and Kucera[360] suggested from this that less copper is dissolved nowadays than previously.

This thesis suggests that the *dissolution of corrosion products by rain* is generally *higher nowadays* than in the 1950-60s due to the increased acidity in precipitation since that time (see section 6.4). In addition, it was previously suggested in this dissertation (section 7.9) that the *formation ratio cuprite/cupric salt* has generally *increased*, e.g. as a result of the strongly reduced SO_2 emissions. Such tendencies would imply a *higher cuprite/cupric salt ratio* on outdoor patina *nowadays*.

It is obvious that the general appearance of sculptures has changed as a result of the changed environment during the industrial period as described in section 2. Many observations of light green streaks on sculptures were made in the 1970s when acidity in rain had increased (see section 2.3). Brown and orange vertical areas consisting of cuprite have recently been observed on sculptures from the 1950s in urban areas, which probably indicates an active state of washing-out of cupric salts from the surface.[361] The

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[356] The estimated dissolution of cuprite and brochantite is 0.45 and 700 mg/l respectively at pH=4.5; pK_s(cup)=14.7 and pK_s(broch)=68.8, Smith and Martell, 1976.

[357] Kucera and Collin, 1977; Holm and Mattsson, 1982; Stöckle *et al.*, 1996.

[358] **Paper IV**; Eriksson *et al.*, 1993b.

[359] Calculations by Persson and Kucera, 1996; from Mattsson and Holm, 1968; Stöckle *et al.*, 1996.

[360] Persson and Kucera, 1996.

[361] **Paper II.**

statement that copper roofs and sculptures in low-polluted areas turn green much more slowly nowadays than previously may also signify that green cupric salts form more slowly and dissolve faster.

In a field investigation, the amount of copper in runoff was reported to increase with the amount of rain falling.[362] In another study of outdoor bronze tablets,[363] copper and sulfate concentrations in the runoff were strongly correlated. Moreover, the acidity of the rain and the acidity of the runoff from the surface did not show any correlation. At low pH in precipitation (< 5) a pH increase was generally observed in the runoff, indicating that the rain was neutralized by the dissolution of copper hydroxy compounds on the surface. At higher pH in precipitation, the relation was generally the opposite, indicating that dry deposition of acidifying substances had occurred on the surface.

Some areas on a sculpture, e.g. *horizontal areas* such as the top of the head and the shoulders of a sculpture, are heavily exposed to the acid rain and the dissolution of corrosion products is likely to occur. An estimation of the amount of corrosion products that may be formed on such areas by dry deposition of SO_2, and the amount of brochantite that subsequently may be dissolved by the acid rain, is outlined in Fig. 7.8. These calculations indicate that at 2 ppb SO_2, which corresponds to the average concentration in central Göteborg[364], the amount of brochantite that may form is probably higher than what may be dissolved by the rain. However, in rural areas with lower levels of SO_2, concentrations may only reach 0.15 ppb,[365] and the calculated amount of brochantite forming may then be completely dissolved by the rain. The figure further indicates that, e.g. at $pH = 4.5$ which is a common value in precipitation nowadays, all brochantite formed by dry deposition of SO_2 in rural areas (<0.3 ppb SO_2) may dissolve. Considering that copper sulfates with higher solubility, e.g. $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$ and $CuSO_4{\cdot}xH_2O$, may form as well (see e.g. Figs. 7.5 and 7.6, and reaction [16]), and that the amount of brochantite calculated must be regarded as an overestimate, the total dissolution of cupric salts may occur even at higher pH and higher concentrations of SO_2.

In *vertical parts* of outdoor objects where the rain water is drained in rivulets, the situation may become different. It is estimated[366] that when the rain initially hits the surface, the concentration of sulfate from brochantite dissolved may be higher than the sulfate concentration in rain. This implies that sulfate in rain does not precipitate initially

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[362] Odnevall-Wallinder and Leygraf, 1997.

[363] Meakin *et al.*, 1992.

[364] Luftföroreningar i Göteborg, 1996.

[365] Reported values, e.g: "Botaniska" (park area in Göteborg) 0.9 ppb, "Kungsbacka" (suburban center) 0.5 ppb (from Luftföroreningar i Göteborg, 1996); or down to 0.15 ppb in rural areas (from Forslund and Leygraf, 1997a).

[366] The estimation is based on the equilibrium calculation of the sulfate concentration by dissolution of brochantite at pH 4.5 being $1.6{\cdot}10^{-3}$ M, and assuming that the sulfate concentration in rain is 10^{-4} M.

from solution. As the water in the rivulets gradually becomes saturated copper, hydroxy sulfates may reprecipitate if evaporation occurs. However, dry deposition of SO_2 may also cause acid compounds, e.g. soluble copper sulfate, to form which may acidify the rivulets drained on vertical areas. The visual appearance of vertical streaks on sculptures accordingly seems to have a different character, some lying on top of the patina while others have etched the surface (see Fig. 5.6e).

Since 0.6-3 μmol Cl^-/cm^2 year[367] has been reported to deposit dry on objects in coastal areas, copper hydroxy chlorides may also form (by reactions described in sections 7.8.1 and 7.11.2) in approximately similar amounts as copper hydroxy sulfates, and they may subsequently be dissolved in the same manner (compare Fig. 7.8). Close to the shore, considerably more chlorides may be deposited, resulting in the formation of mainly hydroxy chlorides and faster greening of such objects.

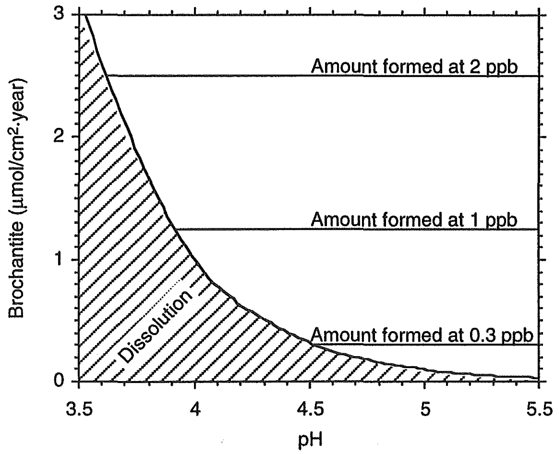

Fig. 7.8 Maximum amount of brochantite formed on an outdoor surface calculated for various concentrations of SO_2 in the air, assuming the deposition velocity to be 1 cm/s (Johansson, 1990) which corresponds to a reactive surface; and the amount of brochantite dissolved by the rain (600 l/m^2 year) for various pH values, assuming all protons are consumed in the dissolution of brochantite. For comparison it may be noted that at the exposure of copper in 69 ppb SO_2 and 500 ppb O_3 at 90% RH, presented in **Paper IV**, brochantite formation corresponded to 3.5 $\mu mol/cm^2$ year.

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[367] Livingston, 1991. Measured on Manhattan.

7.13 Influence of casting, alloy composition and microstructure

7.13.1 Casting

The casting technique, e.g. joints and patches, often becomes apparent when sculptures have been exposed outdoors for several decades. Material from remaining core which has not been removed can escape through pores and cracks, and white spots of plaster from core material may appear on the outside. Brownish stains of rust may indicate iron armature left in the casting, which can cause severe damage to the piece due to volume expansion by corrosion. Iron bolts may suffer from galvanic corrosion.[368]

7.13.2 Alloy composition

The effect of air-pollutants on metals has been the subject of a large number of laboratory investigations and field studies. However, few investigations concern the atmospheric corrosion of copper alloys.[369] Holm and Mattsson studied the atmospheric corrosion of copper and different bronzes in the field, including up to 16-years-long exposures. The authors reported that increasing the tin content in copper alloys tended to inhibit corrosion on rural sites, while no such effect was noted on the urban and marine sites. In a laboratory investigation by Bastidas *et al.* the highest corrosion rate in humid SO_2 environments was observed for a copper alloy containing tin, zinc and lead, the lowest rate being observed for an alloy with tin and lead but no zinc. Bakaliarova *et al.* reported tin bronzes to be most corrosion-resistant, followed by pure copper and brass. Strandberg and Johansson reported that an alloy high in zinc and low in lead exhibited the greatest weight gain when exposed to air-pollutants for four weeks in humid air, while high tin content resulted in low weight increase (Fig. 7.9).

In a field investigation of openly exposed bronze, Meakin[370] reported that zinc was not preferentially dissolved in relation to copper in the runoff. Robbiola[371] observed a selective dissolution by the rain of copper in relation to tin, resulting in a higher tin content in areas of the patina exposed to the rain.

Strandberg *et al.*[372] studied the corrosion by EMPA on bronze samples (Jos II) exposed for four weeks in humid air containing SO_2 and NO_2 (Fig. 7.10). The corrosion product morphology was interpreted in terms of a localised type of attack. The anodic

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[368] Lins, 1983; Strandberg and Rosvall, 1994; Gullman and Törnblom, 1994, pp. 15-24.

[369] **Paper VI**; Riederer, 1972b; Holm and Mattsson, 1982; Bakaliarova *et al.*, 1990; Eriksson *et al.*, 1993a; Bastidas *et al.*, 1995.

[370] Meakin *et al.*, 1992.

[371] Robbiola *et al.*, 1993.

[372] **Paper VI.**

sites were covered by a tin-rich corrosion product close to the metal. On top of this layer, more soluble zinc, copper and sulfur-rich corrosion products formed flower-like outgrowths. The enrichment of tin at the bottom of the corrosion product layer was explained by the oxidation of soluble divalent tin by O_2 to form insoluble $SnO_2 \cdot xH_2O$. The decreased corrosion rate exhibited by copper alloys containing tin is suggested to be connected with the precipitation of $SnO_2 \cdot xH_2O$ on anodic sites.

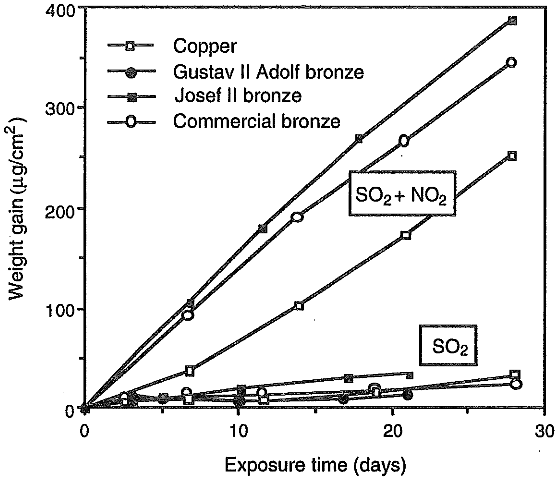

Fig. 7.9 Weight gain of bronze samples exposed at 90% RH to 500 ppb SO_2, or to 500 ppb SO_2 and 500 ppb NO_2. The bronze alloys are described in Table 4.1: GIIA, 91% Cu, 6% Sn, 2% Zn, 0.6% Pb; Jos II, 93% Cu, 1% Sn, 5% Zn, 0.4% Pb; Commercial bronze (Rg 5), 85% Cu, 5% Sn, 5% Zn, and 5% Pb. From **Paper VI.**

7.13.3 Microstructure

The susceptibility to corrosion has been suggested to depend on microstructure.[373] Thus, a copper-rich α-phase was reported to corrode preferentially compared to a tin-rich δ-phase in outdoor atmospheres[374] as well as under marine conditions.[375] On outdoor weathered bronzes, a faster corrosion rate has been observed where pieces of mould have been joined,[376] and patterns of "black islands" and light green pits have been suggested to be related to variations in microstructures.[377] A

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[373] **Paper VI**; Naudé, 1983c, pp. 78-83; MacLeod and Pennec, 1990; Lins, 1992; Robbiola *et al.*, 1993.

[374] Lins, 1992.

[375] MacLeod and Pennec, 1990.

[376] Naudé, 1983c, pp. 78-83.

[377] Robbiola *et al.*, 1993.

chillcast structure has been proposed to resist corrosion better than a coarse-grained structure.[378]

In a laboratory investigation by Strandberg *et al.*,[379] no measurable indication was found that microstructure influenced the corrosion of a chillcast and a tempered material exhibiting only α-phases (Jos II bronze containing 1.4% Sn). However, there was a slight difference in the visual appearance of the two materials studied. The chillcast material exhibited a somewhat darker patina than the tempered material after exposure in a corrosive atmosphere. This may indicate that the formation of cuprite was higher on the chillcast material while the sulfate formation was higher on the tempered material. The difference in visual appearance may also be connected with the higher porosity in the chillcast material. Accordingly, no distinct relation between metallographic structure and corrosion rate was reported on some outdoor sculptures.[380]

Patina on old metal sheets of copper was suggested to be affected by heat treatment and grain size of the material prior to exposure in the atmosphere.[381] Soft copper sheets with large grains, indicating annealing of the material, were light green and exhibited a thick patina layer, while dark patina on tough pitch copper was thinner.

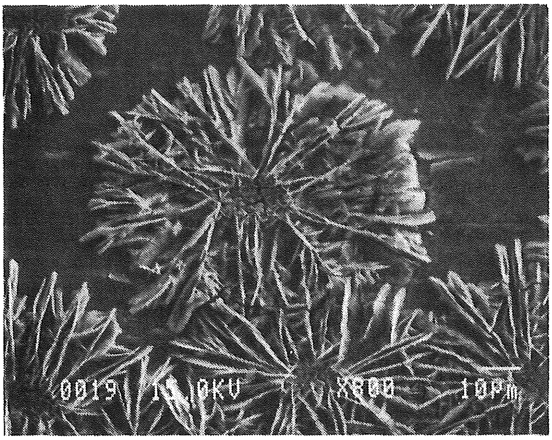

Fig. 7.10 EMPA image of a bronze plate (Jos II) after exposure to 500 ppb SO_2 and 500 ppb NO_2 at 90% RH. Corrosion products are forming flower-like outgrowths on a surface covered with a thin corrosion layer (SEI image). From **Paper VI.**

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[378] Naudé, 1983c, pp. 78-83.

[379] **Paper VI.**

[380] Gullman and Törnblom, 1994, p. 140.

[381] Franey and Davis, 1987.

8 SUMMARY AND CONCLUSIONS

8.1 Cuprite and cupric salt formation

The present laboratory studies reveal the complex corrosion chemistry of copper, corrosion rate and corrosion product composition depending critically on the combination of pollutants. The initial formation of various corrosion products is of fundamental importance for the visual appearance, the subsequent corrosion behaviour and the dissolution of the corrosion products by rain. The formation of a *dark cuprite layer* (Cu_2O) during an early phase of exposure, resulting in a high metal loss, may in a longer perspective be protective and lead to a lower corrosion rate. On the other hand, a corrosion process forming mainly *sparingly soluble* or *soluble green cupric salts* (Cu(II)-compounds) may produce a patina with poorer protective properties, as these compounds may be dissolved or create an electrolyte on the surface. If future laboratory and field studies can enable us to distinguish between the formation of cuprite and cupric salts, efforts to correlate environmental parameters with corrosion may become more successful and results may also be more useful for the understanding of degradation processes in outdoor sculptures.

The air pollution situation has changed during the industrial epoch, and important pollutants such as SO_2 exhibited a culmination during the 1970s in e.g. Sweden. The O_3 and NO_2 concentrations have increased as well during industrialization, but have not declined during the last decades. Nowadays *urban* areas may be roughly characterized by *high* SO_2*+high* NO_2 levels, in contrast to *rural* areas featuring *low* SO_2*+high* O_3 levels.

Laboratory studies show considerable amounts of *cuprite* forming on copper in certain environments (e.g. low SO_2, SO_2+O_3, or with NaCl present on the surface) that may be representative for low-polluted areas, while much less cuprite but more *cupric salts* are formed with other combinations of pollutants (e.g. SO_2+NO_2) that may be predominant in polluted air. A high deposition rate of SO_2 may result in large amounts of *soluble copper sulfate* on the surface as well, and the presence of NaCl may lead to formation of deliquescent *copper chloride* thus creating an acid electrolyte increasing the corrosion.

8.2 Modelling copper and bronze corrosion

Copper and bronze placed outdoors initially turn a *darker brownish shade*, mainly due to cuprite, and a *greenish hue* due to the formation of cupric salts may slowly become discernible. Initially the corrosion process is governed by the interaction of air-pollutants and humidity with the pure metal surface, but later when a patina is obtained the processes of deterioration also involve transformations of compounds in the patina.

The major copper corrosion products found in outdoor patina are cuprite (Cu_2O); the hydroxy sulfates brochantite ($Cu_4(OH)_6SO_4$) and antlerite ($Cu_3(OH)_4SO_4$); and the hydroxy chloride dimorphs ($Cu_2(OH)_3Cl$) atacamite and paratacamite (=clinoatacamite). Additionally, $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$, chalcantite ($CuSO_4{\cdot}5H_2O$) and posnjakite ($Cu_4(OH)_6SO_4{\cdot}H_2O$) have been identified in outdoor patina. Cuprite and brochantite tend to dominate on *rain-washed light green* areas, while several compounds, including copper hydroxy chlorides and antlerite, are found in *dark rain-sheltered* areas. The reactions below demonstrate crucial corrosion processes connected with the dry deposition of pollutants in rain-sheltered areas, and in rain-exposed areas between rain events.

A *high tin content* in a bronze tends to *inhibit* corrosion, a fact which is suggested to be connected with the precipitation of insoluble $SnO_2{\cdot}xH_2O$ on anodic sites. On the other hand, an alloy with *high zinc* and *low lead* content tends to exhibit the *highest corrosion rate* in some corrosive atmospheres.

In some environments corrosion is rapid at 70% *relative humidity*, e.g. when sodium chloride from sea-salt aerosols is deposited on a copper surface, or with synergistic effects of SO_2+O_3. A higher RH is needed to enhance the corrosion process, e.g. for the SO_2+NO_2 synergism which is active only at 90% RH.

At *low* SO_2 concentrations and high humidity, in absence of other air-pollutants, oxidation of copper is very rapid and leads to the formation of a *dull black layer* of cuprite on the surface. Thus, SO_2 may by itself transfer copper into an active corroding state at low levels, while higher concentrations passivate the surface. The results demonstrate that SO_2 is still a decisive factor in outdoor corrosion, even if concentrations have decreased considerably during the last decades in many parts of the world. This is also in agreement with findings from the field where a higher initial corrosion rate has been observed in rural areas than in areas with higher SO_2 concentrations.

NO_2 *or* O_3 in combination with SO_2 strongly enhances corrosion in humid air. At low levels of SO_2, however, the synergistic effect is less marked than at higher levels. O_3 is a more powerful corrosion accelerator than NO_2 and the influences of the two oxidizers are basically different. O_3 in combination with SO_2 results in the formation of massive amounts of *dark cuprite* already at 70% RH, whereas NO_2 combined with SO_2 accelerates corrosion at 90% RH, causes large amounts of *green sulfate* to form, but inhibits cuprite formation. This agrees with results from field investigations reporting on cuprite and sulfates forming in rural areas (low SO_2+O_3), and on sulfate and nitrate in urban areas (high SO_2+NO_2), as well as on diverse corrosion rate behaviours. Thus, various environments may in the long perspective result in patina of different protective properties. Accordingly, some sculptures, sheltered from wind and traffic, e.g. in parks (low SO_2+O_3), have been observed to appear darker brown and to be better preserved than objects exposed to heavy traffic (high SO_2+NO_2) that exhibit more evident green and black colour contrasts.

In *marine* environments, *sea-salt* is deposited on outdoor surfaces. NaCl on copper in humid air results in large amounts of *cuprite*, *red* in colour, in combination with nantokite (CuCl) and *green copper hydroxy chlorides*. Deliquescent copper(II) chloride is also suggested to contribute to an acid electrolyte on the surface. In clean humid air, *tenorite* (CuO) and *malachite* ($Cu_4(OH)_6CO_3$) may also form when chlorides are present. This indicates that these corrosion products may hypothetically be present on copper alloys in marine environments. The reason for not finding these compounds outdoors is suggested to be due to the presence of minute amounts of other species in the atmosphere, such as SO_2, even in relatively unpolluted air. Tenorite, for example, reacts rapidly, acting as an ideal absorber for SO_2, forming copper hydroxy sulfates. The corrosive effect of NaCl is very strong in pure air, as well as in air containing O_3 or SO_2. However, in an atmosphere where SO_2 and O_3 are combined, corrosion is rapid without NaCl, and small additions of salt (typical for inland areas) result in a marked decrease of the corrosion rate, whereas high amounts (characteristic of sites close to the shore) exhibit a similar corrosion rate as when NaCl is absent.

The formation of *antlerite* is favoured by NaCl in SO_2 environments, which agrees with the observation that antlerite and copper hydroxy chlorides often occur together on outdoor copper and bronze objects. Antlerite formation is suggested to be governed by kinetic factors, also indicated by the observation of this corrosion product on older sculptures in outdoor environments. Antlerite is more frequently reported in polluted environments, probably due to higher deposition of SO_2.

8.3 Modelling corrosion of patina compounds

A *cuprite* patina, initially present on copper and bronze objects recently placed outdoors, is rather unreactive towards SO_2 only, but may form *green copper hydroxy sulfates* on the surface if a strong oxidant such as O_3 is present. There are also indications that *carbon* deposits on a cuprite patina may *increase the sulfation* considerably in humid air containing SO_2+NO_2.

Sea-salt deposition on a *cuprite* patina causes the formation of *green copper hydroxy chlorides* on the surface in humid air. Salt addition on cuprite also results in a strongly *enhanced sulfation* when SO_2 is present in humid air. Objects exposed to strong winds from the sea accordingly tend to be more light green on this side, hydroxy chlorides and hydroxy sulfates occurring together.

Copper hydroxy chlorides which are predominant in rain-sheltered areas may convert to *soluble copper sulfate* and probably to *deliquescent copper chloride* when exposed to SO_2 in humid air, which may lead to pitting corrosion. It may be noted that soluble copper sulfate has been detected, and pitting observed, in sheltered areas on old outdoor monuments.

$Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$ may indicate recent *active corrosion* since it is rapidly converted to other hydroxy sulfates in humid air. It is rarely found in outdoor environments but is the most frequently occurring sulfate formed during laboratory studies. It is proposed to be a metastable *precursor* in brochantite and antlerite formation. Whether brochantite or antlerite is formed from this metastable compound is suggested to be determined by e.g. pH on the surface. The scarcity of antlerite in rain-washed areas is tentatively attributed to the washing-out of the precursor, $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$, which exhibits a slightly higher solubility than other hydroxy sulfates, before the slow antlerite formation is obtained.

Brochantite and antlerite do not react in humid SO_2 environments, even when O_3 or NO_2 is present. This kinetic stability is consistent with the frequent occurrence of brochantite and antlerite in outdoor patina. However, a remarkably fast reaction occurs on antlerite and brochantite when *NaCl solution* is added to the surface. This demonstrates that these patina constituents may be converted to *copper hydroxy chlorides*, when *sea salt* is deposited. The combination of hydroxy sulfates and hydroxy chlorides is especially evident in *rain-sheltered areas* on outdoor sculptures where large amounts of sea salt may accumulate.

The patina on *rain-exposed areas* has been reported to consist primarily of brochantite that is unreactive towards SO_2 deposition. However, when sea salt is deposited on the surface, brochantite rapidly converts to copper hydroxy chlorides that are susceptible to deposition of SO_2. The hydroxy chlorides thus may be converted to soluble species, which explains its lack of occurrence in rain-exposed areas. A progressive cyclic weathering is suggested to occur on *brochantite* patina, including: the formation of *hydroxy chlorides* by sea-salt deposition or precipitation; the *conversion to soluble copper sulfate and chloride* by dry deposition of SO_2; and subsequently the *dissolution* and washing-out of the soluble corrosion products by the rain.

8.4 General alterations of patina in outdoor environments

After some decades of outdoor exposure, the first dark cuprite patina generally has developed a patchy and streaked appearance with alternating dark and light green areas. *Rain-sheltered* areas appear *dark and smooth* and best represent the "original surface" of the sculpture. *Rain-washed* areas tend to be *light green* and are more etched. On sculptures from the 1940s and 1950s the patina seems to be in a state of drastic change, exhibiting contrasts between dark and light green areas and distinct vertical streaks. *Orange or brown areas* of cuprite also occur on these sculptures, indicating that compounds in a patina previously darker have been dissolved by the acid rain.

Older sculptures, from the 19th century or the beginning of this century, have thicker corrosion product layers appearing predominantly light green mainly due to brochantite. The high SO_2 concentration in many places during the first part of this century probably caused the formation of thicker cupric salt layers than occurs today. Weathering is dominant in *horizontal parts* of the *light green areas* where rain hits the surface, exhibiting a severely pitted patina where the "original surface" containing tool marks may be completely destroyed, while *vertical green areas* exposed to strong wind are better preserved and may contain other compounds besides brochantite. The corrosion attack implies changed surface qualities even if corrosion is only a few µm/year. In rain-sheltered areas *black crusts* are evident, the coloration being caused by the previously much higher soot content of urban air. The green discoloration on adjacent stone bases of older sculptures indicates the dissolution and washing-out of copper compounds.

8.5 Dissolution of patina compounds

This dissertation suggests that the *formation ratio cuprite/cupric salt* has generally *increased* during the last decades on copper and bronze exposed outdoors, e.g. as a consequence of the strongly reduced SO_2 emissions.

It is also likely that the dissolution of cupric salts by the rain is higher nowadays than during the first part of this century, due to the *higher acidity* in precipitation. This would also tend to give a patina with a higher cuprite/cupric salt ratio.

Calculations suggest that in *rural areas*, the *copper hydroxy sulfates* formed may be completely *dissolved by the rain* nowadays, while the amount of hydroxy sulfates formed in urban areas is probably higher than what may be dissolved by the rain.

8.6 Implications for bronze sculpture conservation

It is obvious that the general appearance of sculptures has altered as a result of the changed environment during the industrial epoch. The formation of *green corrosion* products, and on the other hand also the formation of *black soot crusts* colouring the green corrosion products, probably was faster during *earlier periods of this century* when concentrations of SO_2 and soot were much higher, and when acidity in rain was lower. Accordingly, copper roofs and sculptures placed outdoors *nowadays* are observed to tarnish brown, but are assumed to *turn green more slowly* than previously. Further, on objects remote from traffic, green patina seems to develop more slowly than in central parts of towns where SO_2 and NO_x levels are higher. After a long time of outdoor exposure, however, copper and bronze probably turn green even in unpolluted environments.

The attitude that copper and bronze in outdoor environments *"naturally"* turn *green*, and the expectation for this process to occur, partly reflect the *aesthetic ideal* that developed in industrialized society while the *air pollution* situation grew worse. The evaluation of aged patina on archaeological bronzes in the 19th century also contributed to the appreciation of green patina on outdoor sculptures. In the first phase of industrialization, strong reactions were expressed when monuments became dull black due to the increased burning of coal. Later, the green patina – which also was caused by the increasing air pollution – became much admired, and artificial patination was used to achieve the green "natural" appearance. The appreciation of green patina on sculptures was probably influenced by the Venice Charter from 1964 as well, which emphasized documentary values and considered the monument to remain as a message from the past, including changes over time.

During the 1970s, when attention was focused on the effects of air pollution, the awareness of the problems concerning bronze sculpture conservation increased. The *green, black, patchy and streaked* appearance of sculptures, partly caused by the increasing acidity of the rain, became recognized as a problem in some parts of the world, while another approach maintained the romantic notion that copper turns "naturally" green.

Apprehensions of the appearance of sculptures may differ among individuals and groups of people, as well as regarding different objects, depending on which values are emphasized. By identifying the deterioration process in certain objects, it may be possible to predict future visual changes (e.g. the formation of a green, brown or black patina), and properties that are favoured by decay, conservation or restoration respectively. Properties of significance for cultural objects may be preserved by different interventions, ranging from prevention, maintenance, and consolidation with supportive material, to restoration where the original legibility of the sculpture is revived. General attitudes to interventions may be difficult to formulate since different values may be stressed differently for each object, such as; emotional (e.g. continuity, identity and symbolic values), cultural (e.g. historic, scientific, documentary, aesthetic, artistic, art-historical, and age-values), and use values (e.g. functional, economic, social, and political values). These values have to be identified to preserve and respect the essential message of a specific sculpture. However, general preventive measures and maintenance programmes, especially for new art-works placed and exposed in the corrosive outdoor environment, and deteriorating as demonstrated by these investigations, are urgently needed.

9 FINAL REMARKS AND FUTURE NEEDS

9.1 Direct conservation

Cleaning methods for outdoor bronze sculptures, and surface treatments with coatings, have been developed and discussed during recent decades. Most of the work in this field has been focused on monuments and old sculptures that have not been maintained regularly, but have developed green and black patterns in the patina during the last century's culminating air-pollution situation. Conservation treatments of these sculptures have often been controversial, depending on conflicting views in ethics and aesthetics. Some voices advocate that bronzes remain green, black patchy and streaked, while others call for restoration of sculptures. Strong reactions after conservation activities reflecting diverse values assigned to certain sculptures among groups of people and individuals, as well as the lack of knowledge of deleterious compounds and processes and appropriate surface treatments, have sometimes tended to result in disregard of the problem.

In the professional discussion not much attention has been paid to the modern sculptures. An important question is why we do not maintain new sculptures before they deteriorate and change too much in appearance. Sculptures that are regularly maintained from the beginning by e.g. cleaning and waxing, will probably not suffer a drastic change due to the conservation treatment. If care is considered before the inauguration, the conservator may further have the opportunity to discuss the artist's intent with a still living artist, the patination methods with the foundry, and the location for inauguration of the sculpture. Indeed, if future conservation needs were taken into account already when the artist choses materials and the work is financed, less treatment might well be required.

Sculptures from the 1940s and 1950s have reached a stage of deterioration where the conservation approach may be difficult to judge. Many aspects have to be considered, including values assigned to the sculpture, cleaning methods, application of coatings, economic costs and benefits, reactions from the public etc. The intervention caused by direct conservation measures for older sculptures may be even more strong.

Accordingly, the primary mission should be maintenance programmes especially for new sculptures, to be prepared before sculptures decay in the corrosive outdoor environment. Concurrently as the awareness of the inevitable need to care for all kinds of resources seems to increase in the world, some new tendencies towards care and maintenance are promisingly indicated even for outdoor art.[382]

Fig. 9.1 The conservator on stage. Cleaning of sculptures in the Vigeland Park in Oslo. Photo: Liss Christenssen, 1996.

9.2 Preventive conservation strategies

Preventive measures ought to be considered before sculptures are erected, and maintenance should be performed from the day sculptures are placed outdoors. Preventive strategies have also been emphasized for cultural objects in some recent conferences.[383] Besides many implications, this may be an economical approach.

It may be useful for artists to be aware of long-term effects on their art-works in the outdoor environment, such as the predicted change of appearance and future alterations due to artificial patination. *Discussions with the artist* concerning the intent in relation to changes in the outdoor environment are needed. The artist's intention should further be respected, and to ensure this it must be documented in written form. Communication also ensures that artists understand that conservation will be considered in the future. It may

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[382] See section 2.5.

[383] See e.g. ICOM, 1996.

even help to avoid finishes or design details known to cause problems, e.g. galvanic corrosion.

Communication with bronze casters concerning appropriate methods of artificial patination and surface treatment of sculptures is urgently needed, to deal with future alterations in the corrosive environment. Chemicals and methods used for cleaning, patination and surface treatment of new sculptures in the foundry should be documented for the future. Craftsmen that have worked in many years and may recollect methods used for patination of certain sculptures in the past have invaluable knowledge which has to be documented.

Guidelines for the commissioning of new art-works as a preventive strategy have been designed in Canberra, Australia, to avoid problems in the future.[384] Safety, structural and aesthetic problems, and future conflicts in views between the artist and commissioners could be avoided if such issues were made clear already from the outset.

Outdoor art should be *inspected regularly* by professional conservators, to detect and prevent development of undesirable changes. Regular cleaning and treatment should be conducted by professionals as well.

There are many trustees for public art and it is not always clear who has the responsibility for care of such art. *Information* to the parties concerned is an important step on the path to a preventive approach.

Training programmes for various professionals, working with maintenance of sculptures, should be developed as well.

9.3 Further scholarly-scientific research

Surface treatments

A key issue regarding sculpture conservation is what surface coatings and methods of applications should be used. In Appendix 2 results from a pilot study are presented indicating the reactivity for some conservation products. Much more research and practical experience are needed within this field, especially concerning retreatable methods, e.g. the use of waxes. Protective properties, ageing characteristics, and aesthetic qualities for various waxes must be tested in the laboratory as well as in the field. One question is whether traditional methods of using natural waxes and oils are damaging for bronzes,[385] or whether the formation of copper soaps may provide protective properties to the bronze surface. Another question is what negative long-term effects may be expected from the use of synthetic waxes. Documentation of measures

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[384] Hughes, 1996.

[385] Natural waxes are frequently used in practice, but are also considered to be non-protective; see Burmester and Koller, 1987.

performed, practical evaluation, written publications, communication of good and bad experiences, and open discussions of the use of various products are lacking within this area, as well as in other related fields.

Specific deterioration processes

Birds seem to like sculptures, but cause severe damage by leaving their *bird-droppings* on parts of the surfaces. Besides the disfiguring streaks resulting on the sculptures, droppings cause corrosion due to dissolution of corrosion products. The damage caused by this corrosion process, and various practical preventive measures, e.g. the use of products for partial surface treatment on exposed parts or protection to keep birds away, are essential problems to be solved. In ancient times, sculptures were sometimes crowned by a sharp crescent on the top of the head of the sculpture. Experiments with similar kinds of protection, such as a crown of copper wire, have been carried out.[386] However, some birds do not seem to take flight for anything.

Laboratory investigations

More laboratory studies on the *conversions of patina compounds* should be carried out at various levels of humidity. Cuprite is especially important in this context, since this corrosion product may provide a protective passivating layer on outdoor copper and bronze but may also be destroyed by the corrosive atmosphere, thus exposing the bare metal underneath.

Laboratory studies of corrosion rates and corrosion product compositions of copper and bronze at *low pollutant levels* are needed.

The influence of *carbonaceous particles* on surfaces on the deposition of pollutants should be investigated for copper and patina consituents in the experimental setup presented in this dissertation.

Mechanisms for *"bronze decease"* (symptoms due to chlorides), reactions and critical humidities could be further investigated by controlled laboratory studies.

The original *artificial patination* of sculptures may be crucial for the future appearance. Continuing research is needed to understand the chemical nature of the products of artificial patination, their protective qualities, long-term stability and change in appearance by time. Ways of producing coloured finishes to integrate colour contrasts in patina layers also have to be identified.

More investigations of the *dissolution of patina compounds* are needed from the field as well as from the laboratory, studying the influence of pollutant concentrations and effects in rural, urban and marine atmospheres respectively. The effect of surface treatments on the dissolution of patina compounds is another important issue.

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[386] Refsum, 1996, unpubl.

The unidentified *Phase II* reported in Papers V and VII, should be structurally determined.

The metastable compound $Cu_{2.5}(OH)SO_4 \cdot 2H_2O$ should be characterized regarding solubility and other properties.

9.4 Final remark

To sum up, preventive measures, more scholarly-scientific research and direct conservation measures, especially for new sculptures, are demanded. Concerning the older sculptures, sound considerations and discussions are needed before conservation is executed. In using new architectural copper and in replacing old copper sheets on roofs, aesthetic considerations regarding long-term effects in the outdoor environment should be considered as well.

10 REFERENCES

10.1 Unpublished references

Aineli, M., Outokumpu Copper AB, Västerås. Oral presentation, Seminar in Västerås, June 10, 1997.

Brandberg, J., Miljö Göteborg, Miljöförvaltningen. Personal communication, 1997.

Dolcini, L. Oral presentation,Workshop in Budapest, May 9, 1994.

Elfström-Broo, A., Dept. of Inorganic Chemistry, Göteborg University. Personal communication, May, 1997.

Folmer, A., Architect SAR. Personal communication, June 12, 1997.

Harris, R., Freelance conservator, London. Personal communication, August, 1995.

Hedling, L., Plåtslagerikonsult, Väst AB, Göteborg. Personal communication, May 15, 1997.

Hellberg, S., Gatubolaget, Göteborg. Personal Communication, January, 1993.

Jenssen, O. B., Bevaringssektionen, Nationalmuseet, Brede, Danmark. Personal communication, 1986.

Lindahl, B., Founder, Skånska Konstgjuteriet. Personal communication, April 2, 1993.

Malfilatre, M., Conservator, Bevaringssektionen, Nationalmuseet, Brede, Danmark. Personal communication, May, 1997.

Minne, J. and Bergqvist, B., Founders, Bergmans konstgjuteri, Stockholm. Personal communication, January 15, 1993; March 4, 1993; April 15, 1993.

Outokumpu Copper AB. Discussion, Seminar in Västerås, June 10, 1997.

Pennec, S., Conservator, France. Personal communication, June 6, 1997.

Refsum, S., Conservator, Vigelandmuseet, Oslo. Personal communication, 1996.

Selwyn, L., Ph. D., CCI, Ottawa, Canada. Personal communication, February 3, 1997.

Sommers, J., Curator, The Henry Moore Foundation, Perry Green, UK. Personal communication, August, 1995a.

Sizov, B., Russian Research Institute for Restoration, Moscow. Oral presentation, Eurocare-Copal (EU 316), Workshop in Budapest, May 9, 1994.

Sundberg, M., Outokumpu Copper AB, Västerås. Oral presentation, Seminar in Västerås, May 6, 1997.

Wikborg, T., Curator, Vigelandmuseet, Oslo. Personal communication, June, 1996.

Wikström, L. and Kanerva, M., Conservators, Ars Longa Oy, Helsinki, Finland. Personal communication, May, 1997.

10.2 Bibliography

Abbott, W. H. Effects of industrial air pollutants on electrical contact materials. IEEE Trans. Parts, Hybrids, Pack. PHP-10 (1974) 24.

Alessandrini, G., Dassu, G., Pedeferri, P. and Re, G. On the conservation of the baptistery doors in Florence. *Studies in Conservation* **24** (1979) 108-124.

Alunno-Rossetti, V. and Marabelli, M. Analyses of the patinas of a gilded horse of St Mark's basilica in Venice: Corrosion mechanisms and conservation problems. *Studies in Conservation* **21** (1976) 161-170.

Ammannati, N., Martellucci, E. and Mei, G. Metallurgic characterization of bronze by means of scanning electron microscopy and x-ray microanalysis. In *Verrocchio's Christ and St. Thomas – a masterpiece of sculpture from Renaissance Florence.* Ed. by L. Dolcini, The Metropolitan Museum of Art, New York (1992) 101.

Angelucci, S. La restauration de la fontaine des tortues à Rome. In Proc. *Conservation of Metal Statuary and Architectural Decoration in Open-air Exposure*, Paris, 1986. ICCROM, Rome (1987) 57.

Appelbaum, B. Criteria for treatment: Reversibility. *JAIC* **26** (1987) 65.

Baboian, R. Cliver, B. and Bellante, L. (Eds.). The Statue of Liberty restoration. Proc. *The Statue of Liberty – today for tomorrow conference*, New York, October 1986, NACE, Houston, Texas (1990). 149 pages.

Bakaliarova, E., Timofeeva, N., Kalich, M. and Kassatonova, I. Alliages de cuivre fonderie d'art. Etude en matière de corrosion. *ICOM Committee for Conservation Triennial Meeting*, Dresden, Vol. 2 (1990) 711.

Bartok, W. and Sarofim, A. (Eds.). Fossil fuel combustion. A source book. John Wiley & Sons, Inc. (1991).

Bastidas, J. M., Alonso, M. P., Mora, E. M. and Chico, B. Corrosion of bronze by acetic and formic acid vapours, sulphur dioxide and sodium chloride particles. *Materials and Corrosion* **46** (1995) 515.

Beale, A. The varying role of the conservator in the care of outdoor monuments: Ethical dilemmas. In Proc. *Sculptural Monuments in an Outdoor Environment*, Philadelphia, November 1983. Ed. by V. N. Naudé, Pennsylvania Academy of Fine Arts (1983) 39.

Beale, A. Conservation of outdoor sculpture: an overview. In Proc. *Dialogue/89-, The conservation of bronze sculpture in the outdoor environment: A dialogue among conservators, curators, environmental scientists, and corrosion engineers*, Houston, Texas, 1989. Ed. by T. Drayman-Weisser, NACE (1992) 3.

Bernardini, G. P., Corazza, M., Lalli, C., Matteini, M., Moles, A., Nepoti, M. R., Olmi, F., Sabelli, C., Tosini, I. and Trosti-Ferroni, R. Preliminary technical analysis. In *Verrocchio's Christ and St. Thomas – a masterpiece of sculpture from Renaissance Florence*. Ed. by L. Dolcini, The Metropolitan Museum of Art, New York (1992) 105.

Block, I., Jensen, N., Sommer, S. M. and Buckingham, W. F. Chloride leaching from outdoor bronzes. *ICOM Committee for Conservation Triennial Meeting*, Dresden, Vol. 3 (1990) 1057.

Blomé, B. Kyrkorestaurering i teori och praxis. Humanistiska fakulteten, Konstvetenskapliga institutionen, Göteborgs Universitet, Göteborg, Doctoral dissertation (1977).

Brendel, K., Gruber, C. and Mach, M. Preliminary analysis, conservation and restoration of bronze monuments in Bavaria. In Proc. from *Eurocare-Copal (EU 316) Workshop, Budapest*, 9 May 1994, Institut für Silicatchemie und Archäometrie, Vienna (1994).

Brimblecombe, P. and Rodhe, H. Air pollution – Historical trends. In Proc. *Air pollution and conservation – safeguarding our architectural heritage*, Rome, 1986. Ed. by J. Rosvall, Elsevier, Amsterdam (1988) 107.

Brunius, T. *Estetik förr och nu*. Liber, Stockholm (1986).

Burmester, A. and Koller, J. Known and new corrosion products on bronzes: their identification and assessment, particularly in relation to organic protective coatings. *Recent Advances in Conservation* (1987) 97.

Burrini, F. and Nenncetti. The restoration of the bronze figures of Christ and St. Thomas. In *Verrocchio's Christ and St. Thomas – a masterpiece of sculpture from Renaissance Florence*. Ed. by L. Dolcini, The Metropolitan Museum of Art, New York (1992) 25.

Börjesson, S., Lundgren, H., Lindqvist, O. and Rosvall, J. *Ett söndervittrande Göteborg?* Institute of Conservation, Göteborg 1990:1 (1990).

Calvert, J. G. *SO_2, NO and NO_2 oxidation mechanisms: Atmospheric considerations*. Acid precipitation series, Vol. 3. Ed. by J. I. Teasley, Butterworth Publishers (1984). 254 pages.

Cass, G. R. Conservation of bronze sculpture: future needs in environmental assessments. In Proc. *Dialogue/89-, The conservation of bronze sculpture in the outdoor environment: A dialogue among conservators, curators, environmental scientists, and corrosion engineers*, Houston, Texas, 1989. Ed. by T. Drayman-Weisser, NACE (1992) 359.

Chawla, S. K. and Payer, J. H. The early stage of atmospheric corrosion of copper by sulfur dioxide. *J. Electrochem. Soc.* **137** (1990) 60-64.

Cornell, E. *Arkitekturhistoria. Textdel.* Almqvist & Wiksell, Stockholm (1968).

Crutzen, P. J. Ozone in the troposphere. In *Composition, chemistry, and climate of the atmosphere*, Chapter 8. Ed. by H. B. Singh, Van Nostrand Reinhold (1993).

Dolcini, L. Intelligence and harmony in the work of Andrea del Verrocchio. In *Verrocchio's Christ and St. Thomas – a masterpiece of sculpture from Renaissance Florence*. Ed. by L. Dolcini, The Metropolitan Museum of Art, New York (1992) 13.

Dolske, D. A. and Meakin, J. D. Acid deposition impacts on historic bronze and marble statuary and monuments. *Environmental Effects* MP/November (1991) 53.

Drayman-Weisser, T. (Ed.). Proc. *Dialogue/89-,The conservation of bronze sculpture in the outdoor environment: A dialogue among conservators, curators, environmental scientists, and corrosion engineers*, Houston, Texas, 1989. NACE (1992). 390 pages.

Eldering, A., Solomon, P. A., Salmon, L. G., Fall, T. and Cass, G. R. Hydrochloric acid: a regional perspective on concentrations and formation in the atmosphere of southern California. *Atmospheric Environment* **25A** (1991) 2091.

Ericsson, R. and Sydberger, T. Corrosion products formed on copper exposed to humid SO_2-containing atmospheres. *Werkstoffe und Korrosion* **28** (1977) 755-757.

Eriksson, P. and Johansson, L.-G. The role of NO_2 in the atmospheric corrosion of different metals. *10th Scandinavian Corrosion Congress, Stockholm* (1986) 43-48.

Eriksson, P., Johansson, L.-G. and Gullman, J. A laboratory study of corrosion reactions on statue bronze. *Corrosion Science* **34** (1993a) 1083.

Eriksson, P., Johansson, L.-G. and Strandberg, H. Initial stages of copper corrosion in humid air containing SO_2 and NO_2. *J. Electrochem. Soc.* **140** (1993b) 53-59.

Eurocare-Copal (EU 316) Report. Proc. from a *Workshop in Budapest*, 9 May 1994, Institut für Silicatchemie und Archäometrie, Vienna (1994).

Fassina, V. Environmental pollution in relation to stone decay. In Proc. *Air pollution and conservation – safeguarding our architectural heritage*, Rome, 1986. Ed. by J. Rosvall, Elsevier, Amsterdam (1988) 133.

Feilden, B. M. *An introduction to conservation of cultural property.* Ed. by United Nations Educational Scientific and Cultural Organization, Rome (1979).

Feilden, B. A short introduction to conservation of cultural property in Europe. In Proc. *Air pollution and conservation – safeguarding our architectural heritage*, Rome, 1986. Ed. by J. Rosvall, Elsevier, Amsterdam (1988) 55.

Feilden, B. M. A framework for conservation. Manuscript (1991).

Feitknecht, W. Studies on the influence of chemical factors on the corrosion of metals. *Chemistry and Industry,* September 5 (1959) 1102-1109.

Feitknecht, W. and Schütz, W. Contribution à l'étude chimique de la corrosion du cuivre en solution de chlorure de sodium. *Rév. Métallurgie* **LII** (1955) 327.

Fenger, J. *Luftfororening – en introduction.* Teknisk forlag, Danmark (1985).

Finlayson-Pitts, B. J. and Pitts, J. N. *Atmospheric Chemistry: Fundamentals and experimental techniques.* John Wiley and Sons, New York (1986). 1098 pages.

Fiorentino, P., Marabelli, M., Matteini, M. and Moles, A. The condition of the 'door of paradise' by L. Ghiberti. Tests and proposals for cleaning. *Studies in Conservation* **27** (1982) 145-153.

Fontana, M. *Corrosion engineering.* Materials science and engineering series, 3rd ed., McGraw-Hill Book Co., Singapore (1987). 556 pages.

Forshell, H. *Bronze cannon analysis.* Report no. 2, Armémuseum, Stockholm (1984).

Forshell, H. *Bronzes. Composition – protection.* Report no. 4, Armémuseum, Stockholm (1990).

Forslund, M. and Leygraf, C. Humidity sorption due to deposited aerosol particles studied in situ outdoors on gold surfaces. *J. Electrochem. Soc.* **144** (1997a) 105.

Forslund, M. and Leygraf, C. In situ weight gain rates on copper during outdoor exposures. Dependence on airborne pollutants and climatic parameters. *J. Electrochem. Soc.* **144** (1997b) 113.

Forster, K. W. Monument/memory and the morality of architecture. *Oppositions* (1982) 2.

Franey, J. P. and Davis, M. E. Metallographic studies of the copper patina formed in the atmosphere. *Corrosion Science* **27** (1987) 659-668.

Galloway, J. N. Acid deposition: perspectives in time and space. In Proc. *Acid Reign '95*, June 1995, Göteborg. Ed. by P. Grennfelt *et al.*, Kluwer Academic Publishers, Dordrecht, Netherlands, Vol. 1 (1996) 15.

Gaspar, P., Gulbransen, L. and Weil, P. D. Recent developments in the conservation of outdoor bronze monuments. *ICOM Committee for Conservation Triennial Meeting*, Vol. 23/12 (1978) 1-7.

Gettens, R. J. Composition of the patina on a modern bronze statue. *Technical Studies in the Field of Fine Arts* **2** (1933) 31-33.

Graedel, T. and Franey, J. Formation and characteristics of the Statue of Liberty patina. In book, The statue of liberty restoration. In Proc. from *The Statue of Liberty – today for tomorrow conference*, New York, October 1986. Eds. R. Baboian *et al.*, NACE, Houston, Texas (1990) 101.

Graedel, T. E. Copper patinas formed in the atmosphere – II. a qualitative assessment of mechanisms. *Corrosion Science* **27** (1987a) 721.

Graedel, T. E. Copper patinas formed in the atmosphere – III. A semi-quantitative assessment of rates and constraints in the greater New York metropolitan area. *Corrosion Science* **27** (1987b) 741.

Graedel, T. E. The corrosivity of the atmosphere: past, present and future. In Proc. *Dialogue/89-, The conservation of bronze sculpture in the outdoor environment: A dialogue among conservators, curators, environmental scientists, and corrosion engineers*, Houston, Texas, 1989. NACE (1992) 13.

Graedel, T. E., Benkovitz, C. M., Keene, W. C., Lee, D. S. and Marland, G. Global emissions inventories of acid-related compounds. In Proc. *Acid Reign '95*, June 1995, Göteborg. Ed. by P. Grennfelt *et al.*, Kluwer Academic Publishers, Dordrecht, Netherlands, Vol. 1 (1996) 25.

Graedel, T. E., Nassau, K. and Franey, J. P. Copper patina formed in the atmosphere – I. Introduction. *Corrosion Science* **27** (1987c) 639.

Gudmunsson, G. Plåttak i fara. In *Mest om järn.* Svenska Turistföreningens Årsbok 1989. Ed. by E. Janson, Almqvist & Wiksell tryckeri, Uppsala (1988) 90.

Gullman, J. and Törnblom, M. *Bronze sculpture – Its making and unmaking*. Ed. by Central Board of National Antiquities, Stockholm (1994). 185 pages.

Harris, R. The treatment of outdoor metal sculpture in the United States. *Conservation News, UKIC* **54** (1994) 15.

Hawkins, D. T. The restoration of metal monuments: A bibliography, 1933-1986. *Corrosion Science* **27** (1987) 771-782.

Hedin, L., Granat, L., Likens, G., Buishand, A., Galloway, J., Butler, T. and Rodhe, H. Steep declines in atmospheric base cations in regions of Europe and North America. *Nature* **3367** (1994) 351.

Henriksen, J. and Fossestøl, B. Corrosion by SO_2 in Sulitjelma, a copper mining town in Norway. In Proc. *11th Scandinavian Corrosion Congress, Stavanger*, Norway (1989) F-48.

Henriksen, J. and Rode, A. Corrosion rates of various metals in SO_2/NO_2 polluted atmospheres. In Proc. *10th Scandinavian Corrosion Congress, Stockholm* (1986) 39.

Herrmann, P. Problematik des Korrosionsschutzes von Denkmälern. *Metalloberfläche* **44** (1990) 563-566.

Holm, K. Saly's rytterstatue af Fredrik V. In *Nationalmuseets arbetsmark*, Nationalmuseet og Nyt Nordisk Forlag Arnold Busck A/S, Copenhagen (1981) 88.

Holm, R. and Mattsson, E. Atmospheric corrosion tests of copper and copper alloys in Sweden – 16-year results. In *Atmospheric Corrosion of Metals, ASTM STP 767.* Ed. by J. S.W. Dean and E.C. Rhea, American Society for Testing and Materials, Philadelphia, PA (1982) 85-105.

Hughes, J. Prevention of conservation problems of outdoor sculpture – The importance of the commissioning documentation. *ICOM Committee for Conservation 11th Triennial Meeting*, Edinburgh, Vol. 2 (1996) 876-883.

Hughes, R. Artificial patination. In Proc. *Dialogue/89-, The conservation of bronze sculpture in the outdoor environment: A dialogue among conservators, curators, environmental scientists, and corrosion engineers*, Houston, Texas, 1989. NACE (1992) 231.

Hughes, R. and Rowe, M. *The colouring, bronzing and patination of metals.* van Nostrand Reinhold Company, New York (1983) 1-46.

ICCROM, Proc. *Conservation of Metal Statuary and Architectural Decoration in Open-air Exposure*, Paris, 1986. ICCROM, Rome (1987) 1-297.

ICOM Committee for Conservation 11th Triennial Meeting, Edinburgh, 1996. Ed. by J. Bridgland, James & James, London (1996). 998 pages.

ICOMOS, *Australia ICOMOS charter for the conservation of places of cultural significance (Burra Charter) 1981* (1988).

Jack, J. F. S. The cleaning and preservation of bronze statues. *The Museum Journal* **50** (1951) 231.

Jambor, J., Dutrizac, J., Roberts, A., Grice, J. and Szymanski, J. Clinoatacamite, a new polymorph of $Cu_2(OH)_3Cl$, and its relationship to paratacamite and 'anarkite'. *The Canadian Mineralogist* **34** (1996) 61.

James, P. *Henry Moore on sculpture: a collection of the sculptor's writings and spoken words.* Originally published 1967, Da Capo Press, New York (1992).

Jedrzejewska, H. Some new experiments in the conservation of ancient bronzes. *Recent Advances in Conservation*, IIC, Rome (1961) 135-139.

Jedrzejewska, H. *Konserveringsetik.* Konsthögskolans institut för materialkunskap, Stockholm, Preliminary edition (1980).

Johansson, E. Hur bevara bronsstatyer från korrosion? *Ytforum* **16** (1995) 2.

Johansson, L.-G. Synergistic effects of air pollutants on the atmospheric corrosion of metals and calcareous stones. *Marine Chemistry* **30** (1990) 113-122.

Johnson, B. and Püringer, J. The Orpheus group in Stockholm – building statics in the care and preservation of monuments. *Wiener Berichte über Naturwissenschaft in der Kunst* **4/5** (1987/88) 182.

Jokilehto, J. Conservation principles and their theoretical background. In Proc. *Air pollution and conservation – safeguarding our architectural heritage*, Rome, 1986. Ed. by J. Rosvall, Elsevier, Amsterdam (1988) 83.

Jokilehto, J. Authenticity: a general framework for the concept. In Proc. *Nara Conference on Authenticity*, Nara, Japan, November, 1994. Ed. by K. Larsen, UNESCO, Paris, Agency for Cultural Affairs, Tokyo (1995) 17.

Kalish, M. K. Investigation on protective properties of artificial patina on bronze artefacts. *ICOM Committee for Conservation Triennial Meeting*, Venice, Vol. 25/5 (1975) 1-10.

Kalish, M. K. The use of oxide films to protect monumental copper and bronze sculpture from atmospheric corrosion. *ICOM Committee for Conservation Triennial Meeting*, Zagreb, Vol. 23/14 (1978) 1-6.

Kim, Y. L. The conservation of Jacques Lipchitz's 'Song of the vowels'. *AIC Preprints Boston* (1977) 83-91.

Knotkova, D., Gullman, J., Holler, P. and Kucera, V. Assessment of corrosivity by short-term atmospheric field tests of technically important metals. *Int. Congress on Metallic Corrosion*, Toronto, June 1984, Vol. 3 (1984) 198-205.

Kucera, V. and Collin, M. Atmospheric corrosion with special regard to short-term variations – an investigation using electrochemical and weight loss methods. In *6th European Congress on Metallic Corrosion*. Society of Chemical Industry, London (1977).

Kucera, V., Knotkova, D., Gullman, J. and Holler, P. Corrosion of structural metals in atmospheres with different corrosivity at 8 years' exposure in Sweden and Czechoslovakia. *International Congress on Metal Corrosion Madras*, India, Vol. 1 (1987) 167.

Kuhn, T. S. *The structure of scientific revolutions*. Ed. by O. Neurath, in International Encyclopedia of Unified Science, 2nd ed., University of Chicago Press, Chicago, Vols. 1 and 2 (1970). 210 pages.

Lagerqvist, B. and Rosvall, J. A system approach to the management of photographs and other information sources within the conservation field. *Information Services & Use* **15** (1995) 325.

Larsen, K. (Ed.). Proc. *Nara Conference on Authenticity*, Nara, Japan, November, 1994. UNESCO, Paris, Agency for Cultural Affairs, Tokyo (1995). 427 pages.

Ledheiser, H. *The corrosion of copper, tin and their alloy.* New York (1979).

Lehmann, J. Corrosion of monuments and antiquities made of copper and copper alloy in out-door exhibits. *ICOM Committee for Conservation Triennial Meeting,* Madrid, Vol. 2/5 (1972).

Lemaire, R. and Stovel, H. (Eds.). Nara document on authenticity. In Proc. *Nara Conference on Authenticity*, Nara, Japan, November, 1994. Ed. by K. Larsen, UNESCO, Paris, Agency for Cultural Affairs, Tokyo (1995).

Lewin, S. Z. A new approach to establishing the authenticity of patinas on copper-base artefacts. In Proc. *Application of Science in Examination of Works of Art*, Boston (1970) 62-66.

Lindström, B. Statyer svartnar vid renovering. *Dagens Nyheter*, 1989-08-17.

Lins, A. Outdoor bronzes: Some basic metallurgical considerations. In Proc. *Sculptural Monuments in an Outdoor Environment*, Philadelphia, November 1983. Ed. by V. N. Naudé, Pennsylvania Academy of Fine Arts (1983) 8.

Lins, A. The cleaning of weathered bronze monuments: a review and comparison of current corrosion removal techniques. In Proc. *Dialogue/89-, The conservation of bronze sculpture in the outdoor environment: A dialogue among conservators, curators, environmental scientists, and corrosion engineers*, Houston, Texas, 1989. NACE (1992) 209.

Lipfert, F. W. Dry deposition velocity as an indicator for SO_2 damage to material. *JAPCA* **39** (1989) 446.

Livingston, R. A. Influence of the environment on the patina of the Statue of Liberty. *Environ. Sci. Technol.* **25** (1991) 1400-1407.

Lobnig, R. E., Frankenthal, R. P., Siconolfi, D. J. and Sinclair, J. D. The effect of submicron ammonium sulfate particles on the corrosion of copper. *J. Electrochem. Soc.* **140** (1993) 1902.

Luftföroreningar i Göteborg. Årsrapport 1993. Miljöförvaltningen, Miljö Göteborg, R 1994:4 (1994)

Luftföroreningar i Göteborg. Årsrapport 1995. Miljöförvaltningen, Miljö Göteborg, R 1996:3 (1996).

Mach, M. and Reinhardt, U. Reifenabrieb in der Patina auf Bronzen im Freien. *Wiener Berichte über Naturwissenschaft in der Kunst,* Doppelband 1987/88, **4/5** (1988a) 220.

Mach, M., Reinhardt, U. and Snethlage, R. Elementverteilungsbilder von Querschnitten durch Bronze- und Kupferpatina von Objekten im Freien. *Wiener Berichte über Naturwissenschaft in der Kunst,* Doppelband 1987/88, **4/5** (1988b) 220.

Mach, M. and Snethlage, R. Die Analyse der Patina von Bronzen im Freien. *Zeitschrift für Kunsttechnologie und Konservierung* **3** (1989) 231.

MacLeod, I. D. and Pennec, S. The effects of composition and microstructure on the corrosivity of copper alloys in chloride media. *ICOM Committee for Conservation Triennial Meeting*, Dresden, Vol. 2 (1990) 732-739.

Magnus, G. Über den Einfluss der Zusammensetzung der Bronzen auf die Erlangung einer schönen grünen Patina. *Dinglers Polytechnische Journal* **172** (1864) 370.

Marabelli, M. Characterization and conservation problems of outdoor metallic monuments. In Proc. *Conservation of Metal Statuary and Architectural Decoration in Open-air Exposure*, Paris, 1986. ICCROM, Rome (1987) 209.

Marabelli, M. The environment and the future of outdoor bronze sculpture. some criteria of evaluation. In Proc. *Dialogue/89-, The conservation of bronze sculpture in the outdoor environment: A dialogue among conservators, curators, environmental scientists, and corrosion engineers*, Houston, Texas, 1989. NACE (1992) 161.

Marabelli, M. and Napolitano, G. Nuovi sistemi protettivi applicabili su opere o manufatti in bronzo esposti all'aperto. *Materiali Strutture – problemi di conservatione*, in press (1990).

Matero, F. G. The conservation of immovable cultural property: Ethical and practical dilemmas. *J. of American Inst. of Conservation* **32** (1993) 15-21.

Mattsson, E. and Holm, R. Grön patina på koppartak. *Metallen, Metallverken* (1964) 1-7.

Mattsson, E. and Holm, R. Properties and applications of prepatinated copper sheet. In Proc. *Precoated Materials*, Leamington Spa, Sheet Metal Industries (1967) 1-5.

Mattsson, E. and Holm, R. Copper and copper alloys. *Metal Corrosion in the Atmosphere ASTM STP 435*, American Society for Testing Material (1968) 187.

Mattsson, E. and Holm, R. Atmospheric corrosion of copper and its alloys. *Atmospheric Corrosion* (1982) 365-381.

Meakin, J. D., Ames, D. L. and Dolske, D. A. Degradation of monumental bronzes. *Atmospheric Environment* **26B** (1992) 207-215.

Merk-Gould, L., Herskovitz, R. and Wilson, C. Field tests on removing corrosion from outdoor bronze sculptures using medium pressure water. *ICOM Committee for Conservation 10th Triennial Meeting*, Washington, Vol. 2 (1993) 772-778.

Muller, A. J. and McCrory-Joy, C. Chromatographic analysis of copper patinas formed in the atmosphere. *Corrosion Science* **27** (1987) 695-701.

Mylona, S. *Trends of sulphur dioxide emissions, air concentrations and depositions of sulphur in Europe since 1880.* Meteorological Synthesizing Centre-West, the Norwegian Meteorological Institute, EMEP/MSC-W report 2/93 (1993).

Nassau, K., Gallagher, P. K., Miller, A. E. and Graedel, T. E. The characterization of patina components by X-ray diffraction and evolved gas analysis. *Corrosion Science* **27** (1987a) 669-684.

Nassau, K., Miller, A. E. and Graedel, T. E. The reaction of simulated rain with copper, copper patina, and some copper compounds. *Corrosion Science* **27** (1987b) 703-719.

Naudé, V. N. AIC code of ethics and standards of practice. In Proc. *Sculptural Monuments in an Outdoor Environment*, Philadelphia, November 1983. Ed. by V. N. Naudé, Pennsylvania Academy of Fine Arts (1983a) 110.

Naudé, V. N. List of outdoor bronze sculptures recently conserved. In Proc. *Sculptural Monuments in an Outdoor Environment*, Philadelphia, November 1983. Ed. by V. N. Naudé, Pennsylvania Academy of Fine Arts (1983b) 88.

Naudé, V. N. (Ed.). Proc. *Sculptural Monuments in an Outdoor Environment*, Philadelphia, November 1983. Pennsylvania Academy of Fine Arts (1983c). 110 pages.

Nielsen, N. Keeping the torch lit. *Materials Performance* **23** (1984) 78.

Nosek, E. M. A new composition of patina from the roof of the Wawel Cathedral. *ICOM Committee for Conservation Triennial Meeting*, Zagreb, Vol. 23/6 (1978).

Odnevall, I. and Leygraf, C. Atmospheric corrosion of copper in rural atmosphere. *J. Electrochem. Soc.* **142** (1995) 3682.

Odnevall-Wallinder, I. and Leygraf, C. A study of copper in an urban atmosphere. *Corrosion Science* (1997), in press.

Oesch, S. and Heimgartner, P. Environmental effects on metallic materials – Results of an outdoor exposure programme running in Switzerland. *Materials and Corrosion* **47** (1996) 425.

Ogburn, F., Passaglia, E., Burnett, H., Krugrer, J. and Picklesimer, L. Restoration of large gilded statues using various electrochemical and metallurgical techniques. *Corrosion and metal artefacts- A dialogue between conservators and archaeologists and corrosion scientists held at the National Bureau of Standards* , U.S. Department of Commerce, Gaithersburg, Maryland, NBS Special Publication 479 (1977) 17-37.

Opila, R. L. Copper patinas: An investigation by Auger electron spectroscopy. *Corrosion Science* **27** (1987) 685-694.

Panhorst, M. Sculpture surveys: a summary of projects completed, in progress, and planned. In Proc. *Dialogue/89-, The conservation of bronze sculpture in the outdoor environment: A dialogue among conservators, curators, environmental scientists, and corrosion engineers*, Houston, Texas, 1989. NACE (1992) 309.

Pardue, D. New technology from the Statue of Liberty Restoration. *Recent Advances in Conservation* (1987) 159.

Perocco, G. *The horses of San Marco – Venice.* Thames and Hudson, London (1979) 1-245.

Persson, D. and Kucera, V. *Metallutsläpp orsakade av korrosion och nedbrytning av olika materialytor. En kunskapssammanställning.* Swedish Corrosion Institute, Stockholm, R 1996:3 (1996).

Persson, D. and Leygraf, C. Vibrational spectroscopy and XPS for atmospheric corrosion studies on copper. *J. Electrochem. Soc.* **137** (1990) 3163-3169.

Persson, D. and Leygraf, C. In situ infrared reflection absorption spectroscopy for studies of atmospheric corrosion. *J. Electrochem. Soc.* **140** (1993) 1256-1260.

Persson, D. and Leygraf, C. Initial interaction of sulphur dioxide with water covered metal surfaces: An in-situ IRAS study. *J. Electrochem. Soc.* **142** (1995) 1459.

Phipps, P. B. P. and Rice, D. W. The role of water in atmospheric corrosion. *American Chemical Society Symp.*, Ser. 89 (1979) 235.

Pichler, B., Vendl, A., Pongratz, S. and Sauer, R. Untersuchungen von Patinaproben des Denkmales Kaiser Joseph II. in Wien. In Proc. from a *Workshop in Budapest*, 9 May 1994. Institut für Silicatchemie und Archäometrie, Vienna (1994).

Pollard, A. M., Thomas, R. G. and Williams, P. A. The copper chloride system and corrosion: a complex interplay of kinetics and thermodynamic factors. In Proc. *Dialogue/89-, The conservation of bronze sculpture in the outdoor environment: A dialogue among conservators, curators, environmental scientists, and corrosion engineers*, Houston, Texas, 1989. NACE (1992) 123.

Pollard, A. M., Thomas, R. G. and Williams, P. A. The stabilities of antlerite and $Cu_3SO_4(OH)_4{\cdot}2H_2O$: their formation and relationships to other copper(II) sulfate minerals. *Mineralogical Magazine* **56** (1992) 359.

Pühringer, J., Johnsson, B. An alternative preservation method for corroded outdoor bronzes. *ICOM Committee for Conservation Triennial Meeting*, Dresden, Vol. 2 (1990) 748-753.

Refsum, S. *Livshjulet av Gustav Vigeland.* Institute of Conservation, Göteborg University, 1996:28 (1996).

Reger, L. L. A national initiative to Save Outdoor Sculpture. In Proc. *Dialogue/89-, The conservation of bronze sculpture in the outdoor environment: A dialogue among conservators, curators, environmental scientists, and corrosion engineers*, Houston, Texas, 1989. NACE (1992) 339.

Rendahl, B., Kucera, V., Norberg, P. and Sjöström, C. *Våt- och torrdeponering av försurande luftföroreningar. Inverkan på byggnadsmaterial.* Korrosionsinstitutet, Stockholm, 1995:3 (1995).

Rice, D. W., Peterson, P., Rigby, E. B., Phipps, P. B. P., Cappell, R. J. and Tremoureux, R. Atmospheric corrosion of copper and silver. *J. Electrochem. Soc.* **128** (1981) 275-284.

Rickett, B. I. and Payer, J. H. Composition of copper tarnish products formed in moist air with trace levels of pollutant gas: sulfur dioxide and sulfur dioxide/nitrogen dioxide. *J. Electrochem. Soc.* **142** (1995) 3713.

Riederer, J. Corrosion damage on bronze sculptures. *ICOM Committee for Conservation Triennial meeting,* Madrid 1972. Vol. 2/5 (1972a).

Riederer, J. Korrosionsschaden an Bronzeplastiken. *Werkstoffe und Korrosion* **23** (1972b) 1097.

Riederer, J. Die Pflege von Bronzeskulpturen im Freien. *Berliner Beiträge zur Archäometrie* **2** (1977) 96-104.

Riederer, J. Der Schutz von Metallskulpturen im Freien vor Umwelteinflussen. *Neue Museums Kunde* **25** (1982) 63-65.

Riegl, A. The modern cult of monuments: its character and its origin. *Oppositions* (1982) 21.

Riss, D. Managing the care of outdoor metal monuments by the National Park Service: Some past experience and future direction. An unofficial view by NPS conservator. In Proc. *Sculptural Monuments in an Outdoor Environment*, Philadelphia, November 1983. Ed. by V. N. Naudé, Pennsylvania Academy of Fine Arts (1983) 29.

Robbiola, L., Fiaud, C. and Pennec, S. New model of outdoor bronze corrosion and its implications for conservation. *ICOM Committee for Conservation 10th Triennial Meeting*, Washington, Vol. 2 (1993) 796-802.

Robbiola, L. and Hurtel, L.-P. Nouvelle contribution à l'étude des mécanismes de corrosion des bronzes de plein air: caractérisation de l'alteration de bronzes de Rodin. *Mémoires et Études Sci. Revue de Metallurgie,* Decembre (1991) 809.

Rodhe, H., Langner, J., Gallardo, L. and Kjellström, E. Global scale transport of acidifying pollutants. In Proc. *Acid Reign '95*, June 1995, Göteborg. Ed. by P. Grennfelt *et al.*, Kluwer Academic Publishers, Dordrecht, Netherlands, Vol. 1 (1996) 37.

Roidl, E. Restaurierung- und Konservierungsmethoden bei Bronzen im Freien. *Maltechnik-Restauro* 4 (1987) 9.

Rosvall, J. Air pollution and conservation. In Proc. *Air pollution and conservation – safeguarding our architectural heritage*, Rome, 1986. Ed. by J. Rosvall, Elsevier, Amsterdam (1988a) 25.

Rosvall, J. Introduction to air pollution and conservation. In Proc. *Air pollution and conservation – safeguarding our architectural heritage*, Rome, 1986. Ed. by J. Rosvall, Elsevier, Amsterdam (1988b) 5.

Rosvall, J., Engelbrektsson, N., Lagerqvist, B. and van Gich, J. International perspectives on strategic planning for research and education in conservation. In Proc. *Convegno internationale di studi 'Giovanni Secco Suardo. La Cultura del restauro tra tutela e conservazione dell'opere d'arte'*, Bergamo (1995).

Rozenfeld, I. L. Mechanism of corrosion acceleration by sulfur dioxide and chlorine gas, chloride ions and hydrogen sulfide. In *Atmospheric Corrosion of Metals.* Ed. by E. C. Greco, NACE, Houston, Texas (1972) 125.

Rådström, A. Konstgjutarens hantverk. In *Mest om järn.* Svenska Turistföreningens Årsbok 1989. Ed. by E. Janson, Almqvist & Wiksell tryckeri, Uppsala (1988) 164.

Römich, H. New conservation methods for outdoor bronze sculptures. *European Cultural Heritage Newsletter on Research* 7 (1993) 61-64.

Scott, D. Bronze disease: A review of some chemical problems and the role of relative humidity. *JAIC* **29** (1990) 193.

Scott, D. The microstructure of tin bronzes. In *Metallography and microstructure of ancient and historic metals*, The Getty Conservation Institute, J. Paul Getty Trust (1991).

Seinfeld, J. H. *Atmospheric Chemistry and Physics of Air Pollution.* John Wiley and Sons, New York (1986).

Selwyn, L., Binnie, N. E., Poitras, J., Laver, M. E. and Downham, D. A. Outdoor bronze statues: analysis of metal and surface samples. *Studies in Conservation* **41** (1996) 205.

Sharkey, J. B. and Lewin, S. Z. Conditions governing the formation of atacamite and paratacamite. *The Am. Mineralogist* **56** (1971) 179.

Sherwood, S. The greening of American monuments: The role of atmospheric chemistry in the corrosion of outdoor bronzes. In Proc. *Dialogue/89-, The conservation of bronze sculpture in the outdoor environment: A dialogue among conservators, curators, environmental scientists, and corrosion engineers*, Houston, Texas, 1989. NACE (1992) 33.

Shreir, L. L. (Ed.). *Corrosion.* Vol. 2: Corrosion control. George Newnes Limited, London (1963).

Sinclair, J. D. and Weschler, C. J. Effects of acid rain on indoor zinc and aluminium surfaces. *Am. Chem. Soc. Symposium 318.* Ed. by R. Baboian, Washington DC, Chapter 14 (1986).

Smith, R. M. and Martell, A. E. Critical stability constants: Inorganic complexes. Plenum Press, New York, Vol. 4 (1976).

Socha, J., Lesiak, M., Safarzynski, S. and Lesiak, K. Oxide coating in the conservation of metal monuments: the column of the king Sigismundus III Waza in Warsaw. *Studies in Conservation* **25** (1980) 14.

Sommers, J. Gilding the Lily: The patination of Henry Moore's bronze sculpture. In Proc. *From Marble to Chocolate. The conservation of modern sculpture*, Tate Gallery, London. Ed. by J. Heuman, Archetype Publications (1995b) 144.

Song, I., Rickett, B., Janavicius, P., Payer, J. H. and Antonio, M. R. In situ total-electron-yield sulfur K-edge XAFS measurements during exposure of copper to an SO_2-containing humid atmosphere. *Nucl. Instr. and Meth. in Phys. Res.* **A360** (1995) 634.

Strandberg, H. *Patina på bronsstatyer.* Diploma thesis, The School of Conservation, The Royal Academy of Fine Arts, Copenhagen (1986).

Strandberg, H. Reactions of copper patina compounds – I. Influence of some air pollutants. Submitted to *Atmospheric Environment* (1997a). Paper VII.

Strandberg, H. Reactions of copper patina compounds – II. Influence of sodium chloride in the presence of some air pollutants. Submitted to *Atmospheric Environment* (1997b). Paper VIII.

Strandberg, H. and Johansson, L.-G. The formation of black patina on copper in humid air containing traces of SO_2. *J. Electrochem. Soc.* **144** (1997a) 81. Paper III.

Strandberg, H. and Johansson, L.-G. Role of O_3 in the atmospheric corrosion of copper in the presence of SO_2. *J. Electrochem. Soc.* **144** (1997b) 2334. In press. Paper IV.

Strandberg, H. and Johansson, L.-G. Some aspects of the atmospheric corrosion of copper in the presence of sodium chloride. *J. Electrochem. Soc.* Accepted for publication. Paper V.

Strandberg, H., Johansson, L.-G. and Lindqvist, O. The atmospheric corrosion of statue bronzes exposed to SO_2 and NO_2. *Materials and Corrosion* (1997) November or December issue. Accepted for publication. Paper VI.

Strandberg, H., Johansson, G. and Rosvall, J. Outdoor bronze sculptures – a conservation view on the examination of the state of preservation. *ICOM Committee for Conservation Triennial Meeting*, Edinburgh, Vol. 2 (1996) 894 (Paper II).

Strandberg, H., Langer, V. and Johansson, L.-G. Structure of $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$; a novel corrosion product of copper. *Acta Chem. Scand.* **49** (1995) 5 (Paper I).

Strandberg, H. and Rosvall, J. *Bronsskulpturer utomhus i Göteborg – en undersökning av bevarandetillståndet.* Institute of Conservation, Göteborg University, 1994:16 (1994).

Stöckle, B., Fitz, S., Mach, M., Pöhlmann, G. and Snethlage, R. Die atmosphärische Korrosion von Kupfer und Bronze im Rahmen des UN/ECE-Expositionsprogramms. Zwischenbericht nach 4-jähriger Bewitterung. *Werkstoffe und Korrosion* **44** (1993) 48.

Stöckle, B., Krätschmer, A., Mach, M. and Snetlage, R. *Corrosion attack on copper and cast bronze. Evaluation after 8 years.* UN ECE ICP on effects on materials, Bavarian State Conservation Office, Munich (1996) Draft report.

Sydberger, T. and Vannerberg, N.-G. The influence of the relative humidity and corrosion products on the adsorption of sulfur dioxide on metal surfaces. *Corrosion Science* **12** (1972) 775-784.

Tatti, S. A. Bronze conservation: Fairmount park, 1983. In Proc. *Sculptural Monuments in an Outdoor Environment*, Philadelphia, November 1983. Ed. by V. N. Naudé, Pennsylvania Academy of Fine Arts (1983) 58.

Tidblad, J. and Leygraf, C. Atmospheric corrosion effects of SO_2 and NO_2: A comparison of laboratory and field exposed copper. *J. Electrochem. Soc.* **142** (1995) 749.

Tidblad, J., Leygraf, C. and Kucera, V. Acid deposition effects on materials: Evaluation of nickel and copper. *J. Electrochem. Soc.* **138** (1991) 3592.

Timofeeva, N., Kassatonova, I., Arakelian, F., Bakaliarova, E. and Sizov, B. Etudes complexes du monument à Minime et Pojarski. *ICOM Committee for Conservation Triennial Meeting*, Dresden, Vol. 2 (1990) 754.

UNESCO. International charter for the conservation and restoration of monuments and sites (Venice Charter) 1964. *Erder* (1978).

van Gigch, J. *System design modelling and metamodelling.* Plenum, New York (1991).

van Gigch, J. P. The formulation of strategic management policies for the discipline of conservation. *Board of trustees meeting of Eurocare*, Karlsruhe, Germany (1992).

van Gigch, J. P., Rosvall, J. and Lagerqvist, B. Setting a strategic framework for conservation standards. *Standards for preservation and rehabilitation,* ASTM STP 1258. Ed. by S. J. Kelley, American Society for Testing and Materials, West Conshohocken, USA (1996) 64.

Vendl, A., Sauer, R. and Pichler, B. Untersuchungen an Patina- und Metallproben von Figuren des Milleniums-Denkmales in Budapest. In Proc. from a *Workshop in Budapest*, 9 May 1994, Institut für Silicatchemie und Archäometrie, Vienna (1994).

Vernon, W. H. J. A laboratory study of the atmospheric corrosion of metals. *Transactions of Faraday Society* **27** (1931) 255.

Vernon, W. H. J. The open-air corrosion of copper. Part III. – Artificial production of green patina. *J. Institute of Metals* **49** (1932) 153-167.

Vernon, W. H. J. and Whitby, L. The open-air corrosion of copper. A chemical study of the surface patina. *J. Institute of Metals* (1929) 181-202.

von Feitknecht, W. Über den Zusammenbruch der Oxydfilme auf Metalloberflächen in sauren Dämpfen und den Mechanismus der atmospherischen Korrosion. *Chimia* **6** (1952) 3.

Wayne, R. *Chemistry of atmospheres. An introduction to the chemistry of the atmospheres of earth, the planets, and their satellites.* Oxford University Press, New York (1985) 1-361.

Weil, P. D. Problems of preservation of out-door bronze sculpture: Examination and treatment of the 'meeting of the waters' in St Louis, Missouri. *Bullentin AIC,* **14** (1974) 84.

Weil, P. D. The approximate lifetime of Incralac on outdoor bronze sculpture. *ICOM Committee for Conservation Triennial Meeting*, Venice, 22/2 (1975).

Weil, P. D. A review of the history and practice of patination. *NBS Special publication 479;* US Department of Commerce, corrosion and metal artefacts (1977) 77.

Weil, P. D. The conservation of outdoor bronze sculpture: A review of modern theory and practice. *AIC Preprints, San Francisco* (1980) 129-140.

Weil, P. D. Conservation of bronze sculpture: A series of case studies. In Proc. *Sculptural Monuments in an Outdoor Environment*, Philadelphia, November 1983. Ed. by V. N. Naudé, Pennsylvania Academy of Fine Arts (1983) 67.

Weil, P. D. 'Visually illiterate' and 'historically ignorant': The need to re-examine art conservation's humanistic foundations. *AIC preprint* (1984) 1-14.

Weil, P. D. Conservation of metal statuary and architectural decoration in open-air exposure: an overview of current status with suggestions regarding needs and future directions. In Proc. *Conservation of Metal Statuary and Architectural Decoration in Open-air Exposure*, Paris, 1986. ICCROM, Rome (1987) 1.

Weil, P. D., Gaspar, P., Gulbransen, L., Lindberg, R. and Zimmerman, D. The corrosive deterioration of outdoor bronze sculpture. In *Science and Technology in the Service of Conservation*, IIC preprints, Washington (1982) 130.

Wikström, L. A view of sculpture conservation in Finland. In Proc. *Sculpture Conservation: Preservation or Interference?*, Liverpool 1994. Ed. by P. Lindley, Scolar Press (1995) Chapter 17. In press.

Woods, T. L. and Garrels, R. M. Phase relations of some cupric hydroxy minerals. *Economic Geology* **81** (1986) 1989-2007.

Wuketits, F. M. Synthetic and analytical thinking. *Fresenius Z. Anal. Chem.* (1987) 320.

Young, J. F. Humidity control in the laboratory using salt solutions – A review. *J. Appl. Chem.* **17** (1967) 241.

Zakipour, S., Tidblad, J. and Leygraf, C. Atmospheric corrosion effects of SO_2 and O_3 on laboratory-exposed copper. *J. Electrochem. Soc.* **142** (1995) 757.

Zelst, L. v. and Lachevre, J.-L. Outdoor bronze sculpture: Problems & procedures of protective treatment. *Technology and Conservation* **8** (1983) 18-24.

Appendices

Appendix 1:
Some properties of copper patina compounds

Formation of $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$

In the course of laboratory studies of the atmospheric corrosion of copper or bronze, $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$ was identified as the first copper hydroxy sulfate to appear, in humid air containing ppb amounts of SO_2.[1-4] The corrosion product has also been detected in outdoor environments on bronze sculptures.[5,6] The preparation, characterization by XRD and FTIR, and structural determination of $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$ was presented in Paper I.[7] This appendix describes some additional properties of this copper hydroxy sulfate.

Results

$Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$ was identified as the initial phase formed:
– when tenorite was treated in 2.0 mM $CuSO_4{\cdot}5H_2O$ at 20°C. During prolonged reaction time, brochantite was detected after seven days.
– when tenorite was treated in a saturated solution of $CuSO_4{\cdot}5H_2O$;
a) at 20°C with agitation. Posnjakite or brochantite was detected after seven days.
b) at 40°C without agitation. Antlerite was detected after 12 days.
c) at 70°C without agitation. Posnjakite was detected after two days.

Tentative experiments indicate that $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$ is appreciably more soluble than brochantite and antlerite.

Conclusion

The initial formation of $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$, as observed, suggests the compound to be a likely metastable precursor to brochantite, antlerite and posnjakite in ambient conditions.

XPS studies of copper hydroxy sulfates

Experimental

X-ray photoelectron spectroscopy (XPS) analysis of some copper hydroxy sulfates frequently occurring as corrosion products was carried out. The compounds studied were antlerite, brochantite and $Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$, prepared as described in section 3.2.1.

Powders were gently pressed to thin discs in a pellet compressor and mounted on a gold-plated base with graphite adhesive. A MgK_α (1256 eV) anode was used causing less charging of the sample than the AlK_α source. The total power dissipation was reduced to 250 W to avoid decomposition of the compounds by heating. The analyzed sample area was 0.5 mm^2 (d = 0.8 mm) at a take-off angle of 45°. Survey scans, and multiplex scans for high-resolution information of S(2p), O(1s) and Cu(2p), were performed. All photoelectron peaks were normalized assuming the C(1s) peak from hydrocarbon contamination to be located at 284.8 eV.

The separation of the two photoelectron peaks $2p_{1/2}$ and $2p_{3/2}$ of sulfur was determined by analyzing the spectrum of pyrite (FeS_2). A monochromatic X-ray source, AlK_α (1486.6 eV), was used at a total power dissipation of 350 W. The $2p_{1/2}$:$2p_{3/2}$ area relation was taken to be 1:2 corresponding to the electron population of the respective levels. The peak separation was found to be 1.2 eV.

Results

Table 1 lists the sulfur, oxygen and copper XPS binding energies for the copper hydroxy sulfates. The compounds exhibited nearly identical XPS spectra in the presented analysis.

Table 1 Binding energies (eV) for copper hydroxy sulfates using XPS.

Compound	$S(2p_{3/2})$	O(1s)	$Cu(2p_{2/3})$
Brochantite	168.6	531.8	934.9
Antlerite	168.8	531.9	935.0
$Cu_{2.5}(OH)_3SO_4{\cdot}2H_2O$	168.8	531.8	935.0

All photoelectron peaks are normalized assuming the C(1s) peak from hydrocarbon contamination to be located at 284.8 eV.

References

1. P. Eriksson, L.-G. Johansson and H. Strandberg. *J. Electrochem. Soc.* **140** (1993) 53.
2. H. Strandberg and L.-G. Johansson. *J. Electrochem. Soc.* **144** (1997) 2334. In press. **Paper IV.**
3. H. Strandberg and L.-G. Johansson. *J. Electrochem. Soc. J. Electrochem. Soc.* Accepted. **Paper V.**
4. H. Strandberg, L.-G. Johansson and O. Lindqvist. Submitted to *Materials and Corrosion.* **Paper VI.**
5. H. Strandberg, G. Johansson and J. Rosvall. In Proc. *ICOM Committee for Conservation 11th Triennial Meeting*, Edinburgh, Vol. 2 (1996) 894. **Paper II.**
6. L. Selwyn *et al., Studies in Conservation* **41** (1996) 205
7. H. Strandberg, V. Langer and G. Johansson, *Acta Chem. Scand.* **49** (1995) 5. **Paper I.**

Appendix 2:

A pilot study on the effects of air-pollutants on protective coatings for bronze sculptures

Objectives

The patina on bronze sculptures can be protected from deleterious deposition of air-pollutants by various plastic and wax coatings. Effectiveness of conservation material can be evaluated by e.g. studies of SO_2 deposition. The objective of this pilot study was to investigate SO_2 deposition and weight gain of copper samples treated with some products used for bronze sculpture conservation.

Experimental

The products investigated were polythene wax, microcrystalline wax, paraffin and Incra lacquer. The products were dissolved in solvents according to Table 1, and were applied to polished copper samples (25 x 40 x 1.25 mm) with a brush. The samples were dried in ambient air for two weeks until constant weight was registered.

The experimental setup is described in detail in section 3.2.2. Samples were exposed in air containing 560 ppb SO_2 and 500 ppb O_3 at 95% RH. Deposition of SO_2 was studied during 20 hours' exposure. Weight gain was recorded during four weeks' exposure.

Table 1 Conservation products investigated and solvents, and the colour change of treated copper samples after the four-week exposure.

Product	Solvent	Colour change after exposure
Polyethylene wax	White spirit A[2]	no
Incra lacquer	Toluene	no
Microcrystalline wax A[1]	White spirit A	(not exposed)
Microcrystalline wax B[1]	White spirit B[3]	grey spots
Paraffin	White spirit B	grey spots

[1] Products from two different suppliers
[2] Liav 200
[3] Swedish "lacknafta"

Results

All the samples treated with conservation products exhibited a decreased SO_2-deposition rate (Fig. 1) and a lower weight gain (Fig. 2) than the untreated copper.

The SO_2-deposition rate after 20 hours, and the weight gain after the four-week exposure, were correlated for the conservation products investigated. The relative order according to Figs. 1 and 2 was as follows: Incra lacquer < paraffin wax < microcrystalline wax A < polyethylene wax < microcrystalline wax B < untreated copper.

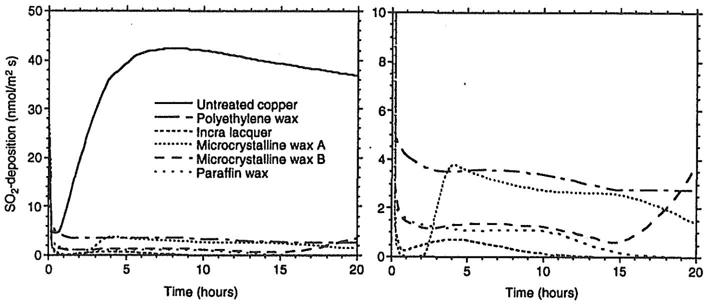

Fig. 1 SO_2 deposition on copper treated with different conservation products in an atmosphere containing 560 ppb SO_2 and 500 ppb O_3 at 95% RH. The close-up figure to the right shows the differences in deposition on the treated samples more clearly.

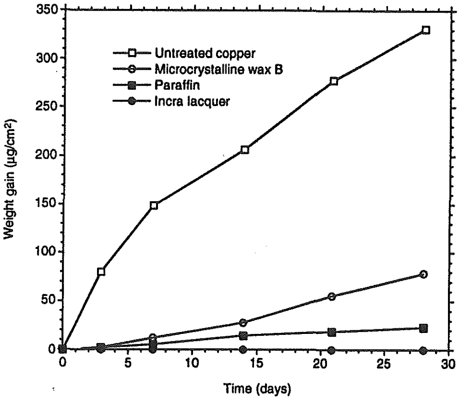

Fig. 2 Weight gain on copper treated with different conservation products in an atmosphere containing 560 ppb SO_2 and 500 ppb O_3 at 95% RH.

Conclusion

Copper samples treated with conservation products showed the following order of SO_2 deposition and weight gain: Incra lacquer < paraffin wax < microcrystalline wax A < polyethylene wax < microcrystalline wax B < untreated copper.

Jag borde väl också

redan här i livet

ha en staty –

jag skulle

proppa den full

och spränga den med dynamit!

För allt slags dödkött

känner jag avsky,

men jag dyrkar

allt som är liv!

Majakovskij

Ur dikten "Jubelfest" 1924

Paper I - VIII

not included in
this edition