CORROSION

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SOURCE BOOK

A collection of outstanding articles from the technical literature

American Society for Metals • National Association of Corrosion Engineers

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A collection of outstanding articles from the technical literature

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DEDICATION

To Elsa and Karen, Kenneth, Monica, Valerie, and Marshall,

and

to C. P. Larrabee for initiating studies, and me, to the weathering steels, and to S. C. Lore for introducing them worldwide while supporting my studies.

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FOREWORD

During the presidency of Franklin D. Roosevelt and the slow ascent of the Defense Department in his administration as the war clouds of Europe were developing, and most significantly since the Pauly Report of the late 1940's, every new president is briefed upon assuming office concerning the state of our defenses and our ability to control any military threat. The key elements in that report deal with our requirements for chromium, nickel, cobalt, zirconium, titanium, uranium, copper, zinc, phosphate rock, etc., and of more recent concern, natural gas and low sulfur crude oil.

Interestingly, none of the foregoing has any significant impact on our ability to erect buildings or construct highways, raise cattle or grow farm crops. On the other hand, without the family of stainless steels or the chemical process industry, oil refinery operations, pharmaceutical plants, food processing companys, and fertilizer and pulp and paper plants would be severely handicapped. Given a little time our steel bridges, transmission towers, automobiles, highway signs and guard rails, bicycles, etc., would rust away slowly from atmospheric attack unless properly maintained.

To prevent this breakdown, a small cadre of chemists, chemical engineers, electrical engineers, metallurgists, bacteriologists, and materials engineers exists as a core group of "corrosion scientists and engineers" dedicated to the understanding of the deterioration of materials. This group, by virtue of its specialized knowledge, is now formulating the concepts, theories, and experiments necessary to shed light on this vexing problem which can seriously affect our life style. Such items as sophisticated aircraft and automobiles, television sets and personal computers, X-rays and CAT scanners along with the mundane steel bridges, transmission towers, and highway signs and guardrails constructed from a variety of processed raw materials could suffer for lack of parts and replacements.

In this kaleidoscope of life the laws of thermodynamics cannot be repealed. Carbon steel structures under appropriate conditions of exposure will deteriorate. The protective coatings have a finite service life. The metallic coatings applied to steel have a longer service life but a finite life nevertheless. Design engineers, while recognizing the physical limitations of a material in a structure or in a piece of equipment, must enhance their knowledge concerning the corrosion aspects of the materials they specify. As it is a near impossibility to "major" in two fields simultaneously while in college, and similarly impossible during the working years, it becomes the responsibility of thoughtful people such as the technical societies to expedite the spread of knowledge.

I consider it an honor and a privilege to have been invited to construct one small bridge to man's accumulated knowledge in the field of corrosion mitigation. This Source Book is an invitation to all its readers to assume the moral and intellectual responsibility to aid in the conservation of nature's resources for today and tomorrow.

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PREFACE

This Source Book is designed to present "case histories" of metal failures caused by the severity of the environment and/or the lack of understanding by the design engineer of the nature of the corrosion process. It has been stated by lubrication engineers that improper lubrication is the cause of a vast amount of damage to operating machinery and, therefore, the cause of much loss to the gross national product. Workers in the sophisticated fields of metal fatigue and fracture mechanics also point to the large monetary losses caused by a lack of awareness of the operating principles of these disciplines. But it remained for the National Bureau of Standards (NBS) together with aid from Battelle-Columbus to establish an approximate loss due to corrosion of $82 billion in 1975. This came to 4.9 percent of the gross national product. The 1971 Hoar Report in England indicated corrosion losses equivalent to 3.5 percent of their GNP. It is estimated that with our present knowledge, $33 billion, amounting to 2 percent of our GNP, can be saved.

To simplify the learning curve and spread some of this knowledge, the American Society for Metals and the National Association of Corrosion Engineers have cooperated in the preparation of this Source Book. The assumption has been made that the readership has a grasp of the fundamentals of general inorganic chemistry from which the electrochemical theory of corrosion derives its support. A literature survey was made to seek out case history type articles in the belief that such a presentation is the quickest means for informing engineers, metallurgists, designers, college engineering students and the general reader concerning the nature of corrosion and the means available for its prevention.

While research in the field of corrosion science is necessary to advance our knowledge at the fundamental level, fortunately the existing principles established by the early giants such as Luigi Galvani (1737-1798), Alessandro Volta (1745-1827), Sir Humphry Davy (1778-1829), and Michael Faraday (1791-1867) remain as the foundation for problem solving efforts today. Therefore, this Source Book is intended to serve in outline form as a textbook of sorts. While the principles of corrosion technology are being presented in a painless form, "shop floor" articles were selected not for their date of publication, but for their illustrative value and their continuing utility. Because of the types of articles sought and the attention to corrosion principles paid by the authors, the collection came principally from the publications of the National Association of Corrosion Engineers.

We begin with the statement concerning the eight visual forms of corrosion by a pragmatic teacher who indicates that virtually all corrosion failures result from carelessness by the user and poor choice of materials or configuration by the designer. This is followed by a description of these forms by a supplier of water treatment chemicals. There follows a discussion of the primary sources of corrosion, namely, the atmospheres: urban, rural, marine and those in between, including the soil. Attention is called to the ongoing testing by committees of the American Society for Testing and Materials who sponsored joint corrosion studies as early as 1906.

Back in the mid-1920's meetings were held at the NBS to consider the serious problems caused by the intense corrosion of underground piping by D. C. traction current. A solution was sought by encasing the pipes in a wire mesh. The idea was based on the recommendation made by Sir Humphry Davy in 1826 to protect the iron hulls of the British Navy by attaching bars of zinc. Thus was born the first commercial use of cathodic protection whose subsequent use has resulted in enormous savings not only in numerous underground applications but, also, in numerous seawater applications such as offshore oil drilling platforms. The successful application of this technique supports Uhlig's contention that "Cathodic protection is perhaps the most important of all approaches to corrosion control." Five papers are devoted to this subject.

The next most impressive and significant means for the protection of steel structures from corrosion deals with the interiors of pipes and chemical equipment exposed to fluid flow where corrosion is controlled with inhibitors. Imagine periodically adding no more than a few parts per million of a substance to prevent attack of a potable water system, or an automotive antifreeze, or a refinery operation to prevent premature replacement. Inorganic inhibitors range from the simple silicates, phosphates and molybdates to simple soaps and complex organic nitrogen compounds. Five papers have been included to illustrate the wide-ranging effectiveness of this remarkable approach to corrosion control.

So long as carbon steel continues as the workhorse for such structures as buildings, bridges, light standards, transmission towers and the like, it requires protection from the elements. One of the most durable approaches is to coat it with zinc by the galvanizing process. Sheet steel is coated on high-speed lines while large objects are coated by immersion in molten baths of zinc. The coating thickness varies from 1 to 5 mils; the service life ranges upwards of 50 years depending upon the environment. Five papers are devoted to the use of zinc as a protective coating.

Aluminum also can be used as a structural material where engineering design justifies. And, like steel, aluminum has a variety of compositions that contribute to its versatility in different atmospheres and under different loading conditions. Like other metals, aluminum can be misused owing to a lack of familiarity with its chemical resistance to different chemicals. And, like zinc, it can be applied to steel sheet on a high-speed line to make aluminized steel having refractory properties as well as weather resistance. The latest development is to combine aluminum with an almost equal quantity of zinc in a high-speed line to produce a coated steel product combining the qualities of both metals to make steel a more versatile product. It is licensed worldwide under the name Galvalume by Bethlehem Steel Corporation.

One of the more remarkable developments in post World War II metallurgy is the expanding use of the HSLA compositions, more familiarly known as the high-strength low-alloy steels under the trade mark USS COR-TEN steels produced by United States Steel Corporation and licensed worldwide. The writer has great familiarity with these steels having been involved from field testing and early use in railroad hopper cars to their presently expanding use in bridges, buildings, transmission towers and highway applications. Because of their rich earthy colors, they have become a favorite medium for sculptors. The subject is covered in four papers.

The stainless steels were discovered by German and English metallurgists at about the same time shortly before World War I. Because of their exceptional corrosion resistance and satisfying appearance, they have found wide application from building exteriors to restaurant sinks. But, more significantly, their resistance to corrosion has made possible the manufacture of numerous pharmaceuticals and sensitive organic compounds that cannot tolerate contamination by trace quantities of heavy metals from equipment corrosion. The most important characteristic of which users of some stainless steels must be aware, however, is their propensity to exhibit stress corrosion cracking under certain circumstances that only now are being more carefully defined. Much effort has gone into the study of this phenomenon which all metals experience under appropriate conditions. One of the newer techniques being used to study the condition with stainless steels is that of anodic polarization. Several papers addressing the problem have been included.

No survey of protective practices of metals would be complete without a thorough discussion of the role of paints. This term, in the minds of many, has a connotation of being decorative in function. But over the past 30 years through the efforts of the Steel Structures Painting Council and the action of many paint producers, the true function of paint has been that of a "protective coating." Few people stop to realize that a thin film—no more than two to five mils thick—of a soft organic resin that is easily scratched can provide resistance to the abuse of wind and rain, sun and airborne dust, and temperature fluctuations every 24 hours, and can continue to serve effectively from five to ten or more years. Research has shown the importance of proper surface preparation, the importance of primers and tie coats, and the use of synthetic top coats formulated from complex polymers. To make the systems more sophisticated, inhibitive pigments and reactive chemicals are incorporated so that chemical reactions occur at the point of application on the substrate. A collection of papers has been included to inform the reader of the factors that must be understood to obtain optimum performance from the entire system.

As a result of the presence of American soldiers in Australia during World War II, a little known protective coating development was brought to the United States in 1949 and modified for the American market. According to one of the early American investigators, the "inorganic zinc coatings have been one of the technological developments of our time which have made a positive impact on society." His reference is to the use of 90-95 volume percent zinc dust mixed into sodium silicate or silicate derivatives to form an inorganic zinc-rich coating that has great abrasion and atmospheric resistance, as well as resistance to a large number of organic compounds. To effect good adherence the steel substrate must present a "white metal" condition. Were an organic zinc-rich composition to be used, then a "commercial" blast condition would be satisfactory. Both zinc-rich systems serve in the capacity of primers; however, the inorganic system can be very effective without a topcoat. Because of a widespread interest in this subject, seven papers were selected.

In any metallurgical treatment of the subject, one cannot fail to pay heed to a failure mechanism alluded to earlier, namely, that of stress corrosion cracking. Unfortunately, there are few warning signs because corrosion is not immediately evident, just the resultant cracking. Stainless steel when stressed to 80 percent of its yield strength will stress crack in a chloride environment at high temperatures. Fracture will occur at locations where stress has been imposed, such as at welds or at the site of bending. Aluminum can stress crack under similar conditions. Copper is susceptible in the presence of ammonia and organic amines or any nitrogen compounds capable of being converted to an amine. Carbon steel is vulnerable in the presence of alkalies and nitrates. To relieve stress, heat treatment has proved helpful; shot peening with glass beads has proven valuable, too. Because of the importance of this subject, six papers were selected for review.

One of the lesser known, though important considerations, is that of hydrogen embrittlement. As one investigator put it, "Hydrogen is like dust in the house—it is extremely difficult to get rid of completely, and everything that is done seems to produce a little." Laboratory experiments have shown that the amount of hydrogen necessary to cause damage is often beyond the limits of detection. Two papers are devoted to this subtle problem.

Copper and its alloys are important metals; however, they suffer from two problems that are not well-known: cavitation and fluid velocity. A paper describing each of these characteristics is included.

Piling is very important in construction. On land it is used in the form of H-piles and pipe piles, whereas in the water it is commonly used in the form of interlocking sheet piles. Five papers that should be of great interest to architects and design engineers have been devoted to the corrosion aspects.

One of the most costly ongoing problems facing highway engineers is the early deterioration of concrete bridge decks caused by the corrosion of the reinforcing bars due to the use of deicing salts. Research has revealed the mechanism as well as several solutions. These are described in three papers.

A number of special topics that are important from the standpoint of corrosion have been covered by single papers. They involve erosion-corrosion, fasteners, valves, microbial attack, fatigue, solar energy, test procedures, monitoring of corrosion with field instruments, and use of exotic metals and titanium in the chemical industry.

As indicated earlier, blame for many failures was placed on the design engineer. Two papers are intended to show that corrosion can be reduced at the design stage with examples given to prove this contention. The final paper is a review of some classic blunders in which the rules of corrosion prevention obviously were ignored.

To complete this survey through the field of corrosion literature, a list of useful books, handbooks, and journals has been included. Valuable bibliographies also are listed following this preface. These are useful assets in making a literature search should the reader have a problem of the type discussed.

In conclusion, the reader can obtain additional information by attending local, regional, and national meetings of the American Society for Metals and the National Association of Corrosion Engineers.

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CONTENTS

SECTION I: PROTECTION AGAINST CORROSION

SECTION II: SPECIFIC ALLOYS

ZINC

ALUMINUM

HIGH STRENGTH LOW-ALLOY STEELS

STAINLESS STEELS

SECTION III: COATINGS

PROTECTIVE COATINGS