Mechanisms of the Atmospheric Corrosion of Weathering Steel.

Mehmet Baha Kuban

Louisiana State University and Agricultural & Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_disstheses

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_disstheses/4307

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
INFORMATION TO USERS

While the most advanced technology has been used to photograph and reproduce this manuscript, the quality of the reproduction is heavily dependent upon the quality of the material submitted. For example:

- Manuscript pages may have indistinct print. In such cases, the best available copy has been filmed.

- Manuscripts may not always be complete. In such cases, a note will indicate that it is not possible to obtain missing pages.

- Copyrighted material may have been removed from the manuscript. In such cases, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, and charts) are photographed by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is also filmed as one exposure and is available, for an additional charge, as a standard 35mm slide or as a 17”x 23” black and white photographic print.

Most photographs reproduce acceptably on positive microfilm or microfiche but lack the clarity on xerographic copies made from the microfilm. For an additional charge, 35mm slides of 6”x 9” black and white photographic prints are available for any photographs or illustrations that cannot be reproduced satisfactorily by xerography.
Kuban, Mehmet Baha

MECHANISMS OF THE ATMOSPHERIC CORROSION OF WEATHERING STEEL

The Louisiana State University and Agricultural and Mechanical Col. Ph.D. 1986

University Microfilms International 300 N. Zeeb Road, Ann Arbor, MI 48106
PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark √.

1. Glossy photographs or pages √
2. Colored illustrations, paper or print ______
3. Photographs with dark background √
4. Illustrations are poor copy ______
5. Pages with black marks, not original copy ______
6. Print shows through as there is text on both sides of page ______
7. Indistinct, broken or small print on several pages √
8. Print exceeds margin requirements ______
9. Tightly bound copy with print lost in spine ______
10. Computer printout pages with indistinct print ______
11. Page(s) _______ lacking when material received, and not available from school or author.
12. Page(s) _______ seem to be missing in numbering only as text follows.
13. Two pages numbered ______. Text follows.
14. Curling and wrinkled pages ______
15. Dissertation contains pages with print at a slant, filmed as received ______
16. Other__________________________________________________________________________

__________________________________________________________________________

University
Microfilms
International
MECHANISMS OF THE ATMOSPHERIC
CORROSION OF WEATHERING STEEL

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in
Interdepartmental Programs In Engineering

by
Mehmet Baha Kuban
B.Sc., University of Manchester, Institute
of Science and Technology, 1981
M.A.Sc., University of British Columbia, 1983
December 1986
Anama, Babama ve Mehmet Emreye...
ACKNOWLEDGEMENTS

The author wishes to thank his supervisor Dr. A. Raman, for his constructive help and guidance throughout the work. The author is indebted to Dr. R. J. Gale for valuable discussion and contribution to the electrochemical testing part of this dissertation. Special thanks also goes to the other members of the graduate committee. The help of all student workers and graduate students of CAMEL are gratefully acknowledged. Special appreciation is due to Ms. Ozdemir for typing part of the manuscript.

Finally, financial support by La. DOTD and Kaiser Aluminum Foundation are gratefully acknowledged.
**TABLE OF CONTENTS**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vi</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>x</td>
</tr>
<tr>
<td>GENERAL INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>PART ONE:</td>
<td></td>
</tr>
<tr>
<td>ELECTROCHEMICAL TESTING FOR MECHANISMS OF DISSOLUTION AND FILM FORMATION</td>
<td></td>
</tr>
<tr>
<td>1.1 INTRODUCTION</td>
<td>3</td>
</tr>
<tr>
<td>1.2 EXPERIMENTED</td>
<td>40</td>
</tr>
<tr>
<td>1.3 RESULTS</td>
<td>50</td>
</tr>
<tr>
<td>1.4 DISCUSSION</td>
<td>86</td>
</tr>
<tr>
<td>PART TWO</td>
<td></td>
</tr>
<tr>
<td>TRANSFORMATION STUDIES</td>
<td></td>
</tr>
<tr>
<td>ATMOSPHERIC EXPOSURE AND LABORATORY TESTING</td>
<td></td>
</tr>
<tr>
<td>2.1 INTRODUCTION</td>
<td>120</td>
</tr>
<tr>
<td>2.2 EXPERIMENTED</td>
<td>135</td>
</tr>
<tr>
<td>2.3 RESULTS AND DISCUSSION</td>
<td>140</td>
</tr>
<tr>
<td>CONCLUSIONS</td>
<td>173</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>179</td>
</tr>
<tr>
<td>APPENDIX</td>
<td>189</td>
</tr>
<tr>
<td>VITA</td>
<td>191</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1.1.1.</td>
<td>Change of free energy(isobaric potential) in transition of metals to the ionic state...</td>
</tr>
<tr>
<td>1.1.2.</td>
<td>Standard free energies of formation for species of the iron-water system.......</td>
</tr>
<tr>
<td>1.2.1.</td>
<td>Chemical compositions of representative weathering steels..........................</td>
</tr>
<tr>
<td>1.3.1.</td>
<td>Comparison of different weathering steels in terms 'm' and the open circuit potential.</td>
</tr>
<tr>
<td>1.3.2.</td>
<td>Effect of pH 11.5 on 'm' for Grade A and Japanese steel.........................</td>
</tr>
<tr>
<td>1.3.3.</td>
<td>Effect of set potential on the value of 'm'. Grade A steel, 0.1% NaCl...........</td>
</tr>
<tr>
<td>1.3.4.</td>
<td>Effect solution anion on 'm', grade A steel.</td>
</tr>
<tr>
<td>1.3.5.</td>
<td>Electrochemical parameters at different sweep rate for grade A steel in 0.1% NaCl, 1% NaCl................</td>
</tr>
<tr>
<td>1.3.6.</td>
<td>Electrochemical parameters at different sweep rates for phosphoric acid treated samples and in phosphoric acid solutions...............</td>
</tr>
<tr>
<td>1.4.1.</td>
<td>The effect of chloride concentration on m...</td>
</tr>
<tr>
<td>1.4.2.</td>
<td>Comparison of metal loss in accelerated v s. atmospheric tests................</td>
</tr>
<tr>
<td>2.1.1.</td>
<td>Packing sequence of oxygen..........</td>
</tr>
<tr>
<td>2.1.2.</td>
<td>Crystal structures of the oxides and hydroxides of iron.......................</td>
</tr>
<tr>
<td>2.3.1.</td>
<td>Analysis of the IR patterns of rust in fig. 2.3.1..................................</td>
</tr>
<tr>
<td>2.3.2.</td>
<td>Analysis of the IR patterns of akagaenite transformations......................</td>
</tr>
<tr>
<td>2.3.3.</td>
<td>Analysis of IR patterns of lepidocrocite transformations..........................</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>1.1.1.</td>
<td>Relationship between corrosion rate and the thickness of the moisture film</td>
</tr>
<tr>
<td>1.1.2.</td>
<td>Energetical illustration of a material resistance to corrosion</td>
</tr>
<tr>
<td>1.1.3.</td>
<td>Potential-pH diagram for iron-water system</td>
</tr>
<tr>
<td>1.1.4.</td>
<td>A schematic representation of the structure of an electrified interface</td>
</tr>
<tr>
<td>1.1.5.</td>
<td>The experimentally measured Tafel constant</td>
</tr>
<tr>
<td>1.1.6.</td>
<td>Dissolution of a Pt electrode</td>
</tr>
<tr>
<td>1.1.7.</td>
<td>Rates of corrosion of steel, 1) Na₂CO₃, 2) NaHCO₃, 3) NaNO₃, 4) Na₂SO₄, 5) NaCl</td>
</tr>
<tr>
<td>1.1.8.</td>
<td>Dependence of the Cd dissolution rate at constant potential on [KI]</td>
</tr>
<tr>
<td>1.1.9.</td>
<td>Dependence of the desorption rate of I ions at potential -0.335 V on the preliminary polarization potential (-0.174-1, -0.124-1)</td>
</tr>
<tr>
<td>1.1.10.</td>
<td>Schematic representation of the corrosion reaction of iron beneath a precipitate film</td>
</tr>
<tr>
<td>1.1.11.</td>
<td>Bipolarity of precipitate films</td>
</tr>
<tr>
<td>1.2.1.</td>
<td>The simultaneous determination of ferrous and ferric ions in solution by differential pulse polarography (DPP)</td>
</tr>
<tr>
<td>1.2.2.</td>
<td>Effect of the presence of oxygen on a polarogram</td>
</tr>
<tr>
<td>1.2.3.</td>
<td>Purifying system for tank argon gas</td>
</tr>
<tr>
<td>1.3.1.</td>
<td>The definition of 'm', the slope of the i v s. t curve</td>
</tr>
<tr>
<td>1.3.2.</td>
<td>Stabilization of rest potentials, a) grade A steel, b) grade B steel, c) mild steel</td>
</tr>
</tbody>
</table>
1.3.3. Infrared pattern of corrosion product from potentiostatic test, grade A steel, 0.1% NaCl................................. 60

1.3.4. Effect of prior surface treatment on the i vs. t profiles of grade A weathering steel in 0.1% NaCl................................. 61

1.3.5. Effect of specific adsorption of chloride, grade A........................................ 62

1.3.6. Specific adsorption of chloride and the variation of pH, grade A steel.................. 63

1.3.7. Polarographic analysis of potentiostatic test with grade A steel in 0.1% NaCl- unpurged. Bold numbers indicating sampling time in minutes........................................ 64

1.3.8. Polarographic analysis of potentiostatic test with grade A steel in 0.1% NaCl-purged. 65

1.3.9. Polarographic analysis; phosphoric acid treated sample, unpurged.................. 66

1.3.10. Polarographic analysis, phosphoric acid treated sample, purged.................... 69

1.3.11. Method of analysis and calibration plot for polarographic analysis.................. 71

1.3.12. Simultaneous determination of i, E(rp), pH and the ratio Fe(II)/Fe(III) for bare steel in 0.1% NaCl........................................ 72

1.3.13. Simultaneous determination of the four parameters for bare steel in purged 0.1% NaCl........................................ 73

1.3.14. Infrared patterns of the corrosion products from potentiostatic tests with bare grade A steel: a) purged, b) unpurged solution of 0.1% NaCl........................................ 74

1.3.15. Simultaneous determination of the four parameters for phosphoric acid treated samples in 0.1% NaCl........................................ 75

1.3.16. Simultaneous determination of the four parameters in purged 0.1% NaCl solution phosphoric acid trt........................................ 76
1.3.17. Unpurged 25% phosphoric acid solution...... 77
1.3.18. Purged 25% phosphoric acid solution........ 78
1.3.19. E v s. i plot for bare grade A steel in
Ø.1% NaCl. Sweep rates a)0.1 mV/s b)1mV/s... 79
1.3.20. E v s. i plot for bare grade A steel in
1% NaCl. Sweep rates a)0.1mV/s b)1mV/s...... 80
1.3.21. E v s. i plot for phosphoric acid treated
sample in 0.1% NaCl, sweep rate 0.1 mV/s.... 82
1.3.22. E v s. i plot for phosphoric acid treated
sample in 0.1% NaCl, sweep rate 1 mV/s...... 83
1.3.23. E v s. i plot for sample in phosphoric acid
solution, sweep rate 0.1 mV/s................. 84
1.3.24. E v s. i plot for sample in phosphoric acid
solution, sweep rate 1 mV/s................ 84
1.4.1. Weight loss curves for sheltered location
coupons at Leesville bridge............... 115
1.4.2. The effect of displacement from E(oc) on 'm'. 117
1.4.3. Chloride concentration v.s. m ............. 118
1.4.4. IR pattern of atmospheric exposure coupon
surface treated with 25% phosphoric acid.... 119
1.4.5. Schematic model of adsorbed phosphoric acid
molecules separated by adsorbed water
molecules..................................... 119
2.1.1. Projection of the lepidocrocite crystal.
γ-FeOOH is orthorhombic but is based on
a fcc framework of oxygen. The plane of
the figure is (100) of fcc.................... 132
2.1.2. A comparison of γ-FeOOH and spinel structure. 132
2.1.3. Orientation relationship in the transformation
of lepidocrocite(L) to maghemite(M) to
haematite(H).............................. 133
2.1.4. Projection of the hollandite structure....... 133
2.1.5. A drawing of the cigar shaped somatoids of
akaganeite. One of the crystals is blown-up
to show a unit cell.......................... 134
2.2.1. Standard IR patterns of rust phases found in the atmosphere.............................. 138

2.3.1. IR absorption patterns formed on weathering steel surfaces with different surface treatments....................................................... 158

2.3.2. IR absorption patterns of the transformation of akagaenite in air................................................................. 164

2.3.3. IR absorption patterns of the transformation of akagaenite in air................................................................. 167

2.3.4. IR absorption patterns of the transformation of lepidocrocite in air................................................................. 168

2.3.5. SEM micrographs of a) $\gamma$-FeOOH b) $\beta$-FeOOH... 168

2.3.6. X-Ray pattern of two different preparations of $\beta$-FeOOH................................................................. 169

2.3.7. Transformations of $\gamma$-FeOOH in vacuum............. 170
ABSTRACT

The atmospheric corrosion mechanisms of weathering steel have been investigated through the use of both field and laboratory techniques. Laboratory techniques included time-transformation studies of the oxide-hydroxides $\alpha$-FeOOH and $\beta$-FeOOH under controlled temperature conditions in air and in vacuum, as well as electrochemical testing for the characterization of the dissolution and film formation kinetics.

Potentiostatic tests with set potentials in the immediate vicinity of the open circuit potential of the weathering steel were found to simulate very well the conditions of atmospheric exposure. 0.1% NaCl solutions as well as other concentrations were generally used for comparison purposes. The specific adsorption of chloride ions from the solution were found to have a significant influence on the rate of dissolution of the steel. The rate of change of the current with time($m$) was determined at various settings. Potentiodynamic tests were done to verify the dissolution mechanism of weathering steel in chloride media. The effect of the surface treatment of the inhibitor phosphoric acid was also investigated using the same techniques.

The infrared spectroscopic technique was successfully utilised to follow the phase transformations of the
Fe-H$_2$O system both in the laboratory and in field exposure testing. The transformations of akagaenite and lepidocrocite to haematite were confirmed but a previously unreported intermediate, the hydrated maghamite, was found. Ferrihydrite was found to occur in rural atmospheres.
GENERAL INTRODUCTION

The corrosion process of steel has attracted a great deal of interest due to the significance of this metal and the financial losses caused by its degradation. Weathering steels are a family of low alloy steels that were developed for use in structural applications exposed to the atmosphere, such as bridges.

There is a large volume of literature on the atmospheric exposure testing of this material that identifies the corrosion products and their mutual transformations. Studies that combine the characterization of the electrochemical dissolution kinetics in environments simulating atmospheric conditions, with a comprehensive atmospheric testing program, however are not available.

This type of a comprehensive investigation was made possible by a three year program of atmospheric corrosion testing of weathering steels on the highway bridges of Louisiana. This investigation included, therefore, the gathering of large amounts of data from field exposure as well as electrochemical characterization of the corrosion mechanisms of weathering steels. The work that forms the dissertation includes the infrared spectroscopic study of transformations in rust phases both in the field and in the laboratory. The work is presented in two parts: 1) Electrochemical testing for mechanism studies, and 2) Phase transformations-
atmospheric and laboratory testing, which are then joined by the common conclusions.
PART ONE

ELECTROCHEMICAL TESTING FOR MECHANISMS OF DISSOLUTION
AND FILM FORMATION

1.1 INTRODUCTION

Atmospheric corrosion is a significant industrial phenomenon considering the fact that about 80% of all metallic structures are exposed to atmospheric environments. The development of weathering steels with a special combination of alloying elements, that are supposed to enhance the formation of protective rust layers, is an important advancement in technology.

The electrochemical nature of atmospheric corrosion or the deterioration and degradation of the surfaces of metals through charge transfer reactions is a subject that has been investigated and understood quite well (1-5). The important characteristic of the atmospheric environment is that it is mainly moist air with several contaminant species in it, the nature of which will depend on the particular location. Therefore, essentially moisture in contact with the constituents of the atmosphere becomes an ionically conductive fluid which is an electrolyte(6). Storing a metal in vacuum, removes its contact with this conductive medium and thus prevents the charge transfer reactions that spontaneously destabilize its surface.

Due to the great variety of atmospheric environments
experienced even among sites not so far from each other, due to uneven development of land (i.e. rural, urban, industrial, marine etc.) and differences in geography, the conductive electrolyte is particularly difficult to characterize. Atmospheric corrosion, therefore, tends to be an extremely locality-specific process with the nature and chemical composition of the moist atmosphere to a large extent determining the rate and character of the degradation process. Classifications that are generally accepted have been made regarding the different types of wet films that can be obtained on metal surfaces and the different atmospheric corrosion mechanisms associated with them (7). These are the following:

(a) Moisture films due to maximum relative humidities of ~100% associated with rain, sea spray etc.. This would be termed wet atmospheric corrosion and would be visible to the naked eye.

(b) Moist atmospheric corrosion with relative humidities less than 100%. Charge transfer would proceed under an extremely thin, almost invisible moisture film.

(c) Complete absence of film of moisture, hence any atmospheric corrosion.

There is no doubt that all these forms, particularly the first two, could be operating at the same time because wet-dry cycles keep occurring through the effects of rain and sunshine. Figure 1.1.1 roughly illustrates the
relationship between the thickness of the moisture film and an arbitrary corrosion rate.

Of all the types, wet atmospheric corrosion is the one that comes closest in mechanism to electrochemical corrosion in bulk electrolyte. The thinner the film of moisture, the more difficult it becomes to characterize the process in terms of parameters derived from complete immersion.

Many experimental techniques have been developed that are all based on the electrochemical nature of corrosion but also incorporate factors such as wet-dry cycles, relative humidity, atmospheric pollutants etc. One of the important parameters that separates atmospheric corrosion from other types is the time of wetness (tw). This is due to the fact that for charge transfer reactions to occur, the thin electrolyte is essential. The duration that the current flows and the effect on the structural character of the film due to drying by the sun are very important. Several different test methods have been developed based on galvanic cells of alternating copper and iron plates (8-11). These methods can be used to determine tw and measure the instantaneous rate of atmospheric corrosion outdoors. For example, copper wire wound around a rod made from the metal under investigation (12), and thin films of metals deposited on glass substrates, permit calculation of corrosion rates from the change of resistance of current carrying la-
yrs(13). Artificial climate chambers, where the effects of meteorological factors such as low humidity, air temperature, wetting time by phase layers of moisture and chemical composition of atmosphere were all controlled parameters, also have been used(14-17).

Correlation of these tests with actual behavior determined by long exposure atmospheric corrosion tests are sketchy. Friese and Schwenk evaluated the use of laboratory galvanic electrolytic cells and concluded that these electrochemical data cannot be used to determine corrosion properties(18). Sereda came to a similar conclusion after considering sensor readings from test sites(19). Russian workers, however, have reported successful correlation(12,13,15). Mazza et al.(20) found better correlation with atmospheric results. The basic mechanism studies of the corrosion or dissolution of iron and steel have been made using electrochemical techniques in bulk solutions incorporating both in-situ and ex-situ methods of the observation of the metal surface. Much of the extensive data available for iron and steel in different solutions, dissolution, passivation-deposition behaviour, is from the proliferation of more sophisticated surface analysis techniques used together with the traditional electrochemical testing methods.
Equilibrium thermodynamics applied to the stability of metals

Atmospheric corrosion, i.e. instability of a metal in the presence of a thin electrolyte film with air present, from observations of everyday life, is a spontaneous process. It is not difficult to demonstrate that corrosion and degradation of most industrial metals, however ugly or unpleasant they may look, is an attempt to reach a natural equilibrium. Table 1.1.1 shows for a number of important metals the free energy changes that are associated with the transition from neutral to ionic state. The negative sign for the change in the free energy denotes a thermodynamical potential towards a transition to the ionic state; the more negative the change in free energy the greater the potential for change. A positive free energy change would mean a transition that could not be self-sustaining.

It can be seen in Table 1.1.1 that in the presence of oxygen, except for a handful of metals (Au, Ir, Pt, Pd), most metals are unstable thermodynamically and tend to move towards the oxidized state. As a result, these four metals, termed the noble metals, are the only ones found in nature in their pure metallic state; all others occur as their oxides and salts. According to their degrees of stability, judged by the relative value of their change in free energies, the degrees of corrosion resistance of various metals can be described as illustrated in figure 1.1.2.
Misawa(107) has listed the standard free energies of formation of various species of the Fe-H O system, including solid as well as dissolved species; some pertinent values are listed in Table 1.1.2

All species can be seen to have negative free energies of formation with respect to metallic iron.

A more useful way of looking at the function of equilibrium thermodynamics was provided by the so-called pH-potential, or Pourbaix diagrams, after Pourbaix(22). These yield information regarding the stability with respect to pH of ionic states of a metal as well as insoluble oxides or oxide-hydroxides. The data is provided by a calculation of the reversible potentials for a metal that is in equilibrium with its simple ions or soluble products of hydrolysis, or insoluble forms of oxide. Under the given pH conditions, the stable form is that given by the most negative value of the potential. An example of a potential-pH diagram is given in fig.1.1.3.

However, the role of equilibrium thermodynamics ends here due to several reasons.

1) pH values on such diagrams always refer to values in the immediate vicinity of the metal surface.

2) This immediate vicinity pH is not always representative of the bulk property due to the fact that a cathodic reaction also takes place at the metal surface either by consumption of H ion by the hydrogen evoluti-
on reaction;
\[
2H^+ + 2e^- \rightarrow H^2
\]
or, the generation of \(\text{OH}^-\) ions by oxygen reduction;
\[
\text{O}_2 + 2H_2O + 4e^- \rightarrow 4\text{OH}^-
\]
For these reasons, it is not uncommon to observe experimentally a particular hydroxide at a region where the pH-potential diagram forbids it to form. Potential-pH diagrams and the use of equilibrium thermodynamics in predicting corrosion behavior should be used with caution. Thermodynamics, then, determines the essential requirements for corrosion to take place and in which direction it should tend, but the complete picture of the rate of corrosion reactions and the controlling mechanisms cannot emerge without a knowledge of the kinetics or so called electrodics of corrosion.

Before reviewing the various theories and studies that attempt to explain the mechanisms and kinetics of iron dissolution, it is perhaps in place to briefly summarize the basic electrodics, i.e., the terms and reactions that define the events that take place as soon as a metal has been immersed in an aqueous solution.

When a metal is immersed in an electrolyte an interface is created. The arrangement for example, of the water molecules that are essentially randomly oriented and electro-neutral in the bulk of the solution becomes altered by the presence of this interface. The interface thus becomes a region of transition between the crystallographic array of
the solid metal and the random orientation of the bulk electrolyte. Therefore, the random orientation of dipoles and equal distribution of negative and positive charges are altered to a situation where there is a net orientation of solvent dipoles and a net or excess charge on laminae parallel to the electrode surface; in other words the electrolyte side of the interface has become charged. Since the metal consists of charged particles, i.e. a communal pool of mobile negative charge in a 3-D periodic network of positive ions, the electrons quickly react to this field produced by the charging on the electrolyte side of the boundary.

Thus, charge separation has occurred in the interface region, dividing the interface into oppositely charged layers that can now produce a potential difference. The region as a whole, however, remains neutral. The potential differences created are relatively small (~1V) but so are the dimensions of the interface region (~10 Å). The fields created in this interface region, appropriately named the electrical double layer, are thus very big, of the order of $10^7$ V/cm. One can understand the importance of the presence of such an enormous field on the kinetics of the electrochemical processes occurring at metal surfaces.

A schematic of the structure of an electrified interface is given in figure 1.1.4. The first row is occupied by water molecules and the second row by solvated ions, the locus of centers of which is called the outer Helmholtz
plane or (OHP). Some of the less solvated ions in the solution get through the OHP to a position closer to the electrode where they are less solvated. The ionic species that can do this are mostly anions. These achieve contact with the electrode and the locus of their centers form the inner Helmholtz plane, or (IHP). Ions adsorbed in this manner are said to be specifically adsorbed. The nature and strength of specific adsorption naturally changes the character and magnitude of the potential gradient that has been created. It can be easily seen that the electrical double layer will affect the kinetics of charge transfer, which essentially is the corrosion or the metal dissolution rate. The fundamental role that the electrical double layer plays in the stability of metal surfaces, even under thin electrolyte films such as those found as moisture films in atmospheric corrosion, makes it important to understand the relationship between the double layer structure and measurements of macro-parameters such as potentials and currents across interfaces. The special influence anions have due to specific adsorption, particularly chloride ions, is also extremely important. This is because of the presence of various impurities and pollutants that are present in the atmosphere and thus in the moisture films that play the role of electrolyte in atmospheric corrosion.
A corroding metal in a solution corresponds to a short-circuited cell system with cathodic areas where the electrons are consumed and anodic areas where the electrons are produced. These also are called the electron-sink and electron-source areas. The reactions occurring at these areas are called de-electronation and electronation reactions, respectively. These two areas can be thought of as either being fixed in space and time, i.e., heterogeneous corrosion, or random in space and in time, i.e., dynamic or homogeneous corrosion. The latter is also called the Wagner-Traud homogeneous theory of corrosion. In whatever form we think of the sites, the short-circuit character demands that the potential difference across the system be equal to zero. This cell potential consists of the potential difference between the cathodic and anodic regions of electrodes plus the potential drop 'iR' across the solution that connects them. Assuming that $iR \approx 0$, then in the absence of any high resistivity oxide films, one should have $\Delta E_{anodic} = \Delta E_{cathodic}$. The current created by the dissolution of the cathodic metal at the anodic sites and the cathodic current are also equal under the short circuit conditions thus $I = -I_a$ and the corrosion rate is equal to the metal dissolution rate which is $I_a$.

The uniform potential gradient that exists between a corroding metal and its solution is called the corrosion potential $\Delta E_{corr}$ and is given by,
The quantities that define these two, i.e. the corrosion potential and the corrosion rate or current are given by the Butler-Volmer equation of electrochemistry. For the corrosion current,

\[ I_{\text{corr}} = A_i \left[ \exp \left( \frac{\Delta a F}{RT} \eta_{\text{a}} \right) - \exp \left( - \frac{\Delta a F}{RT} \eta_{\text{a}} \right) \right] \]

(1)

where the overpotential is the corrosion potential \( \Delta E_{\text{corr}} \) minus the equilibrium potential for the anodic reaction of metal dissolution (\( E_{\text{a}} \)), \( \text{M}^{n+} + n\text{e}^- = \text{M}_n^{(n-n)} \)

i.e. \( \eta_{\text{a}} = \Delta E_{\text{corr}} - \Delta E_{\text{a}} \)

The \( \alpha \)'s denote the transfer coefficients which are the constants that determine the slope of the log \( i \) versus overpotential plots, i.e. the Tafel slopes of a multistep reaction. \( R, T \) and \( F \) have their usual meanings.

Tafel slopes, which are obtained by the application of the Tafel law, are probably the most important relations in the electrochemistry of corrosion. Tafel simply stated that the potential difference across an interface at which an electrochemical reaction is occurring, changes linearly with the logarithm of the current density. This relation holds for both the anodic and cathodic reactions:

\[ \eta_{\text{a}} = b_0 \log \frac{i_0}{i_{\text{corr}}} \]

(2a)
where the b's are the Tafel slopes of a plot such as the one shown in figure 1.1.5.

The Tafel slopes can be put into the Butler-Volmer equation (1) as well as the exchange current density \( I = i, \theta \), \( a, \theta, a \)

\[
I_{corr} = I_{0,a} \left[ \exp \left( \frac{\eta_a}{b_a} \right) - \exp \left( -\frac{\eta_a}{b_a} \right) \right] \tag{3}
\]

A similar equation can be written for the cathodic reaction:

\[
I_{corr} = -I_c = I_{0,c} \left[ \exp \left( -\frac{\eta_c}{b_c} \right) - \exp \left( \frac{\eta_c}{b_c} \right) \right] \tag{4}
\]

Remembering that \( \gamma = \Delta E \) - \( \Delta E \) for both the anodic and cathodic reactions, by dividing both 3 and 4 by \(-F \Delta E / 2RT\) and equating them, one can obtain an expression for the corrosion potential, \( \Delta E_{corr} \).

How are the observation of these equations, the measurement of \( i \) and \( E \), and the determination of \( I \) Tafel slopes used to elucidate dissolution mechanisms for Fe? What is the overall reaction that precedes film formation? What are the steps when Fe ionizes and goes into solution? What are the soluble, ionic reactants and products, and also by what sequence the steps proceed? Finally what is the particular step that determines the overall rate of dissolution? These have been the critical questions
that researchers have asked and tried to answer. Due however to the universal phenomenon of film formation, later stages of the iron corrosion processes start including reaction kinetics that are influenced and often determined by the reaction of the solution with these products. Phase transformations dictated by specific conditions also have an important influence. In atmospheric corrosion mutual solid state phase transformations of one corrosion product to another, under wet-dry cycling conditions of the atmosphere, become the most important factors determining protection or further corrosion.

Due to the wide use of iron and steel, the corrosion of these materials under various conditions has occupied scientists for a long time. Evans, Uhlig, Frumkin, Tomashev, Akimov, Vetter, Laque, Copson, Pourbaix and many others laid the basic foundations and defined corrosion science as a discipline of its own (23-27).

Various experimental studies attempting to elucidate the elementary steps of the anodic dissolution of iron in different media have made it clear that there exists a Tafel relation between potential and current and the Tafel constants or slopes need to be known for any classification of the mechanisms. Bockris has explained how the Tafel slope (6) yields the mechanism from the determination of the transference constant \( \alpha \).

The transference constant can be used to deter-
mine the rate determining step (RDS) in a multistep reaction. One of the first things recognized was that the rate of dissolution of Fe in acid solution was a function of pH, as was known earlier for alkaline solutions(28). This eliminated consideration of simple mechanisms that were proposed earlier;

\[
\begin{align*}
\text{Fe}^{2+} + 2e^- &= \text{Fe} \\
\text{Fe}^{2+} + e^- &= \text{Fe} \\
\text{Fe} + e^- &= \text{Fe}
\end{align*}
\]

Lorenz et al. (29) suggested that in acid solutions free from oxygen, other oxidising agents and surface active substances, the anodic dissolution of iron proceeds by one of the two different reaction mechanisms that were proposed by Bockris, Drazic and Despic (30),

\[
\begin{align*}
\text{Fe} + \text{H}_2\text{O} &= \text{Fe.H}_2\text{O(ads)} & [1] \\
\text{Fe.H}_2\text{O(ads)} &= \text{Fe(OH)}_{\text{ads}} + \text{H}^- & [2] \\
\text{Fe(OH)}_{\text{ads}} &= \text{FeOH(ads)} + e^- & [3] \\
\text{RDS} \quad \text{FeOH(ads)} &\overset{\text{RDS}}{\longrightarrow} \text{FeOH} + e^- & [4] \\
\text{FeOH} + \text{H} &= \text{Fe} + \text{H}_2\text{O} & [5]
\end{align*}
\]

characterized by a Tafel slope of

\[
b = \frac{2}{3} \times 2.303RT/F = 40 \text{ mV}
\]

and electrochemical reaction order of -1, where the electrochemical reaction order stands for the exponent of the concentration terms in the expression for the reaction rate(6) e.g.

\[
-dC/dt = kC_A^b C_B^c \ldots C_N^n
\]
each exponent in the order of reaction with respect to the species concerned (at constant \(E\)) or,

\[
\left( \frac{\partial \log \text{rate}}{\partial \log c_A} \right)_B \ldots c_N, E = a
\]  

(7)

For electrochemistry this would be,

\[
\left( \frac{\partial \log i}{\partial \log c} \right)_B \ldots c_N, E = a
\]

(8)

For the Fe dissolution reaction,

\[
\left( \frac{\partial \log i_0}{\partial \log c_{H^+}} \right)_E = -1
\]

(9)

as mentioned above.

Heusler et al. (31,32) have put forward an alternative mechanism with \(\theta = 30\text{mV}\) and order of reaction equal to \(-2\). These parameters are yielded by the same set of equations as the Bockris mechanism but [4] is replaced by,

\[
\text{FeOH(ads)} + \text{Fe} = \text{Fe(FeOH)ads} = \text{catalyst} \quad [6]
\]

\[
\text{Fe(FeOH)ads} + \text{OH}^- \rightarrow \text{FeOH} + (\text{FeOH})\text{ads} + 2e \quad [7]
\]

Lorenz et al. have proposed that either mechanism can be followed depending on the structure of the surface (33,34). These authors proposed that the Bockris mechanism was favored by a low density of grain boundaries and other imperfections, such as dislocations emerging at the surface etc., while the Heusler mechanism applied for a high density of imperfections.

The important feature of both mechanisms is the direct participation of hydroxyl ions in the dissolution process for iron in bulk electrolytes that are acidic. This was first suggested by Bonhoeffer and Heusler to explain the
experimental observation that at the same electrode potential, the corrosion rate of iron was lower in acidic solutions than in basic\cite{31}, and decreased even further as the pH was lowered. OH generation in acid solutions is presumed to take place by the dissociation of water at the electrode surface\cite{36-38}.

No agreement between studies have been achieved regarding the value of Tafel constants for mechanism determination. Rojter, Juza and Polujan\cite{39} using 1 M FeSO$_4$ found for the anodic process $a/b$ value between 60 and 75 mV depending on the history of the electrode, whereas Stern and Roth\cite{40} using 4% NaCl, pH 1.50 obtained 68 mV. Okamoto, Nagayama and Sato\cite{41} reported a $b$ value of 100 mV using iron in 3N H$_2$SO$_4$. Hoar and Hurlen\cite{42} found $b=30$ mV in 0.5M FeSO$_4$ solution containing 0.1M NaHSO$_4$. Kaesche\cite{43} obtained $b=30$ mV in NaClO$_4$. Makrides, Komodromos and Hackerman\cite{44} found $b=40$ mV in 2M HCl. Gatos\cite{45} using 1N H$_2$SO$_4$ found $b=60$ mV when the dissolution was produced in the presence of depolarizing agents. Hoar and Holliday\cite{46} and Hoar and Farrer\cite{47} obtained $b$ values in the range 50-70 mV for the dissolution of mild steel in H$_2$SO$_4$ solutions. Makrides\cite{48} found $b=39-60$ mV by dissolving iron in H$_2$SO$_4$ solution. Podesta and Arvia\cite{49} confirmed the Bockris mechanism with similar Tafel slopes in a variety of solutions. Kelly\cite{50} also studied the dissolution of iron in non-inhibiting media. After careful determination of the parameters for
mechanisms, he found the 40 mV to be the Tafel constant and a first order dependence on the concentration of OH\(^-\) ions, consistent with the Bockris mechanism. Furthermore, Kelly claimed that the theoretical basis for the Heusler mechanism, as well as the proposals by Lorenz et al.(33,34) to modify the Heusler mechanism were seriously defective. Further discussion can be found in his original paper(50).

**The effect of electrolyte anions on the dissolution process**

The unusual effect of anions on the anodic dissolution of metals, particularly that of chloride, has been the center of some controversy. Ershler(51) was one of the first to quantify the effect of chloride ion on rates of dissolution. Ershler observed an effect shown in figure 1.1.6. The almost horizontal parts of the curves correspond to the dissolution of the electrode due to the action of a current of constant strength. The values inserted on the curves are microamperes, doubled after each arrest. As can be seen in figure 1.1.6, the dissolution rate of Pt in a 15 N H\(_2\)SO\(_4\) containing 0.4 M HCl at equal potentials appears to be four times greater than in 15 N H\(_2\)SO\(_4\) solution with the addition of 0.1 N HCl. Since there is a greater excess of SO\(_4^{2-}\) ions over Cl\(^-\) ions, the surface concentration of Cl\(^-\) on Pt may be thought of as being directly proportional to the rate of dissolution. Ershler proposed that the slowest step in the dissolution of Pt would probably be the discharge of
Cl ions on a Pt atom with the subsequent formation of a Pt-Cl group followed by the weakening of the bond between Pt and the metal lattice.

Kabanov, Burstein and Frumkin(28) studied the effect of different [Cl-]/[OH-] ratios in solutions of NaOH and concluded that the Cl ions allows Fe to be formed, but does not participate in the process itself. They suggested this arises from the fact that when the concentration of Cl ions in 0.01 N NaOH solution is varied from 0.1 N to 4 N the rate of the process Fe $\rightarrow$ Fe(OH)$^{2+}$ remains unaffected and equal to the rate of the process Fe $\rightarrow$ Fe$^{2+}$ in acid at the same electrode potential. The accelerating effect of Cl ions on the corrosion of iron would thus seem to be due to the fact that it hinders the formation of films by adsorbed oxygen which would otherwise end the dissolution process. These authors thus take the adsorption effect of chloride or other anions to be the way in which these ions influence anodic dissolution.

Earlier on in the investigation of the effects of halide ions, particularly that of chloride ions, Evans took the view that its influence was limited to the penetration of protective films on metals by these aggressive species resulting in the disintegration of the films(52,53). Other workers however, started pointing to a more fundamental way in which halide ions participated in the metal dissolution(54-57).
Rozenfeld stated that an activating effect of aggressive ions can be observed in cases where the metal surface is practically free of a phase film (57). He observed that the anion participated directly in the elementary event of the ionization of the metal, as demonstrated in figure 1.1.7 for the effect of different anions on the general corrosion rate of steel. He envisioned the anodic dissolution of metal to be proceeded by a preliminary adsorption of the anion, consequently forming metal-anion complexes that pass into solution:

\[
Mn^e + mA \rightarrow (m-n)^{-} \rightarrow MA + ne^{-}
\]

Rozenfeld also cautioned against a generalization of this behavior however, proposing that there was probably a critical value of the concentrations and electrode potentials beyond which inhibiting effects would be seen.

Kolotyrkin (58) and co-workers studied the effects of various electrolyte anions on the dissolution of metals. Figure 1.1.8 shows the effect of increasing KI concentration on the dissolution rate of cadmium at constant electrode potential in 1N H₂SO₄ solution and the similar affect of increasing Cl⁻ ion concentration on the dissolution rate of indium amalgam in perchlorate solution.

Another interesting observation by Kolotyrkin was the effect of preliminary polarization potentials on the strength of the adsorption of the anions on the metal surface. Using very low iodine ion concentration and silver as
the electrode, he found out that the desorption from the metal surface of the initially adsorbed I ions behaved as illustrated in figure 1.1.9. Thus, he concluded that the specific adsorption of anions, beginning at far more negative values of the potential than that of electrode dissolution, should be regarded as the beginning of the formation of the corresponding salt (presumably by covalent bonding). Especially at the early stages, there is a considerable difference in the strength of the bonding to the metal surface. From available data it seemed that the direct participation of the electrolyte anions in the elementary act of ionization of metallic atoms was an inevitable step in the process. Kolotyrkin thought that not all the metal-surface complexes would pass into solution, but only whose chemical bond strength has attained a specific, necessary value. The following scheme was envisioned,

\[
\text{Me(O\_\text{H})\_m} + p\text{Cl}\rightarrow \text{Me(Cl)}^{p} + m\text{H}_2\text{O}
\]

\[
p\text{Cl} + 2\text{H}^{+} + \text{MeO} \rightarrow \text{Me(Cl)}^{n+} + n\text{e}^{-}
\]

where the initial adsorbed molecules of water were replaced by the more aggressive Cl ions. This mechanism allowed the formation of a metal-chloride complex which can subsequently pass into the solution. These complexes would be wholly hydrolyzed to form oxygen complexes and free halide ions as the diffusion process goes on. These freed halides would then be available for a re-adsorption process.
Foley (59), in his review of the literature on the effects of chloride on corrosion processes, came to the following conclusions:

a) There is evidence for the penetrating effect of chloride ions into oxide films that are otherwise protective.

b) Chloride ion is adsorbed preferentially on metal surfaces.

c) Adsorbed chloride ions produce a strong electric field that draws ions from the metal.

d) The halide ion act as a catalyst by forming some sort of an intermediate bridging structure.

e) The stability of this metal-halide surface complex determines the kinetics of the corrosion process.

Electro-dissolution kinetics of iron and steel have been studied more so in acidic solutions than in neutral and alkaline solutions. The effect of Cl\(^-\) ion on the Tafel slopes and reaction orders are parameters that help explain the stage at which anions interfere in the elementary ionization steps of the iron. The determinations of these parameters in neutral solutions are directly applicable to corrosion processes, such as corrosion of steel in cement and atmospheric corrosion.

Lorenz and co-workers (60) were the first to propose the following modifications to the elementary ionization reactions of iron in the presence of chloride ions:
Fe + Cl = FeCl ads \[8\]

FeCl ads = FeCl ads Fe + Fe Cl + 2e \[9\]

RDS FeCl ads Fe + OH OH FeOH + Fe + Cl + 2e \[10\] + + 2+

FeOH + H = Fe + H O \[11\]

By assuming reaction \[10\] to be the rate determining step and also surface coverage of FeCl ads approaching unity, the calculated Tafel slopes were 60 mV which agreed well with experimental data. Podesta(61) proposed a reaction sequence analogous to the one above with Tafel slopes of 60 mV also.

Nobe and co-workers investigated dissolution kinetics of Fe in acidic, neutral and alkaline solutions(62-65). They proposed that in acidic chloride solutions, that contained a low H ion concentration, the following reaction schemes would dominate;

- Cl accelerated mechanism;

\[
\begin{align*}
\text{Fe.H O} + \text{Cl} & = [\text{FeClOH}] \text{ads} + \text{H} + \text{e} \\
[\text{FeClOH}] \text{ads} & \rightarrow \text{RDS} \text{FeClOH} + \text{e} \\
\text{FeClOH} + \text{H} & = \text{Fe} + \text{Cl} + \text{H O}  \\
\end{align*}
\]

- OH accelerated mechanism;

\[
\begin{align*}
\text{Fe.H O} & = \text{FeOHads} + \text{H} + \text{e} \\
\text{FeOHads} & \rightarrow \text{RDS} \text{FeOH} + \text{e} \\
\text{FeOH} + \text{H} & = \text{Fe} + \text{H O}  \\
\end{align*}
\]

The surface coverages of FeClOH ads and FeOH ads were assumed to be about 0.8 and almost 0 respectively. They suggested that these two reaction sequences would be opera-
ting in parallel in low \([H^+]\) ion solutions and found Tafel slopes of 75 mV that fitted their empirical relationships.

On the other hand, for high \([H^+]\) ion solutions the empirical rate equations were more consistent with the following sequence which they called the \(H^+\) ion mechanism:

\[
\begin{align*}
\text{Fe.H}^0 + \text{Cl}^- + 2\text{H}^+ &\rightarrow \text{FeClads} + \text{H}_2\text{O} + 2\text{e}^- + 2\text{H}^+ \\
\text{FeClads} + \text{H}^+ &\rightarrow \text{FeClH} + \text{H}^+ + \text{e}^- \\
\text{FeClH} + \text{Cl}^- &\rightarrow \text{FeCl}^{2+} + \text{H}^+ + \text{e}^- \\
\text{FeCl}^{2+} &\rightarrow \text{Fe}^{2+} + 2\text{Cl}^-
\end{align*}
\]

assuming the surface coverage of \(\text{FeCl}^{ads}\) species to be about 1 and \(\text{FeClH}^{ads}\) to be 0. Tafel slopes for this set of equations were found to be about 110 mV.

However, in other work that used not so concentrated acidic chloride solutions, they found Tafel slopes of around 70 mV and used the following sequence to explain it:

\[
\begin{align*}
\text{Fe}^{2+} + \text{Cl}^- + \text{H}^+ &\rightarrow [\text{FeClOH}]^{ads} + \text{H}^+ + 2\text{e}^- \\
[\text{FeClOH}]^{ads} &\rightarrow \text{FeClO}H^- + 2\text{e}^- \quad \text{RDS} \\
\text{FeClO}H^- + \text{Cl}^- + \text{H}^+ &\rightarrow \text{Fe}^{2+} + \text{Cl}^- + \text{H}_2\text{O}^-
\end{align*}
\]

They proposed that this mechanism may be operating at low polarizations. In neutral and alkaline solutions Nobe and co-workers found Tafel slopes of between 60-66 mV and they invoked basically the same mechanism as above except this time the chloro-iron complex was given the stoichiometry \([\text{Fe(OH)}_m(\text{Cl})_n]^{2-m-n}\) with the possibility of a different type of complex in neutral and alkaline solutions.

McCafferty and Hackerman(66) suggested that Nobe et
al.'s mechanism could not be correct due to the fact that they fail to consider that the electrode surface is covered with water molecules. McCafferty and Hackerman found the anodic Tafel slopes of 60 mV in acidic high Cl⁻ solution and used the following scheme;

\[ Fe + H_2O = (Fe.H_2O)_{ads} \quad [25] \]
\[ (Fe.H_2O)_{ads} + Cl^- = FeCl(ads) + H_2O \quad [26] \]
\[ FeCl(ads) + H = FeCl(ads).H = complex \quad [27] \]
\[ complex + H^+ \longrightarrow FeCl(ads) + 2H^+ + 2e^- \quad \text{RDS} \quad [28] \]

Turnbull and Gardner (67) investigated the electrochemical dissolution kinetics of structural steel in 3.5% NaCl solutions and determined anodic Tafel slopes of 50-60 mV.

Kuo and Landolt (68) studied the corrosion of iron in concentrated chloride solutions and observed mass transport limited dissolution current using a rotating disc electrode. They found that the divalent iron ion was the diffusion limiting species and the limiting current conditions corresponded to the saturation concentration of FeCl₂, indicating that under these conditions of limiting current the anode was covered by a thin layer of FeCl₂. The dissolution rate of the FeCl₂ was the rate limiting step.

The later stages of the dissolution of iron and steel do not lend themselves to rapid determination of the kinetic reaction scheme. The reason for this is the formation of a multitude of corrosion products, which have been discussed
with respect to atmospheric corrosion in the next part of this work. As oxide-hydroxide films form and thicken, rate processes become limited by the speed with which charge can be transferred within the films, thus mass transport and diffusion rates start becoming important. The electronic and crystallographic properties of these corrosion products also become important as the film plays the role of physical blockage from the solution and aggressive ions in it.

Sato and co-workers identified the problem of the kinetics of corrosion on steels after the formation of corrosion products in terms of a membrane system(69). They represented the iron corrosion process under a precipitate film as in figure 1.1.10, where the membrane system could be set up as follows;

\[
\begin{align*}
\text{(I)} & : \quad \begin{array}{c}
+ \\
H, OH
\end{array} & - \\
\text{precipitate} & \quad \begin{array}{c}
H, OH \\
n^+
\end{array} & \quad \begin{array}{c}
- \\
Fe, Cl
\end{array} \\
\text{film} & \quad \begin{array}{c}
m^+ \\
Fe, Cl
\end{array}
\end{align*}
\]

where I and II represent the interior phase and the bulk solution respectively.

As the membrane potential of an ion-exchange membrane depends on the fixed charge on the membrane and the mobility, concentration and activity coefficient of ionic species in the membrane phase, they used the multi-ionic membrane potential derived by Dray and Sollner(70). Sato found from his experimental work with ferric hydroxide precipitate film that corrosion product films were ion-selective and, particularly the ferric hydroxide film was anion selective. That
is, after the formation of precipitate films on the surface of metal in a solution of chloride, the anodic current would be carried with the anions from the solution to the metal surface. The membrane potential, otherwise termed the diffusion potential, for such an anion selective film would be given by:

$$E_d = -\frac{RT}{F} \ln \left( \frac{a_{Cl^-}^\Pi}{a_{Cl^-}^I} \right)$$  \hspace{1cm} (10)

and for a cation selective film;

$$E_d = \frac{RT}{F} \left[ \ln \left( \frac{a_{M^+}^\Pi}{a_{H^+}^I} \right) - \ln \left( \frac{u_{H^+} \cdot \gamma_{M^+}^\Pi}{u_{M^+} \cdot \gamma_{H^+}^I} \right) \right]$$  \hspace{1cm} (11)

where u's are transport numbers and γ's are activity coefficients.

Sato et al. proposed that the electrode potential of the electrode included also the diffusion potential as given by eq.10 and 11. In a membrane system such as that above, the diffusion potential would be negative for $a_{Cl^-}^I < a_{Cl^-}^\Pi$ and positive for $a_{Cl^-}^I > a_{Cl^-}^\Pi$. The electrode potential would therefore be pushed to more noble values in the former case. In the latter case, which would correspond to the enrichment of Cl ions under the precipitate films, the electrode potential would shift in the positive direction. This situation was suggested to occur for cases leading to local corrosion such as pitting by the shift of the potential to values that exceeded the depassivation potential.
Influence of phosphoric acid on the electrodissolution kinetics

Phosphates in general belong to the most used corrosion inhibitors for steels in aqueous, nearly neutral solutions. They have been widely used in water systems as potent reducers of section loss. The use of phosphoric acid for surface treatment on weathering steel is not known. In this project the influence of phosphate films on atmospheric rusting is also found to be inhibitory, as witnessed by some of the results of field testing, shown in the next part of this thesis. The effect of phosphates or phosphoric acid on the electrodissolution kinetics can be investigated in two ways, i) by surface treating the surface of the electrode and allowing the phosphoric acid to react with the surface prior to electrochemical testing, or ii) by testing bare weathering steel surfaces in phosphoric acid solutions of the same concentration.

Although kinetic studies of iron are plentiful in hydrochloric acid and sulphuric acid, not much work exists for behaviour in phosphoric acid by itself. The kinetic parameters of electrodissolution of Fe in phosphoric acid were determined by Rajagopalan et al. (71). These workers found an anodic Tafel slope of 60 - 10 mV and found that the anodic dissolution of iron followed the Bockris mechanism
(6), formulated for anodic dissolution in acid solutions. The cathodic Tafel slope was determined to be \(110 - 10\) mV corresponding to the RDS in the hydrogen evolution reaction,

\[
\begin{align*}
\text{H}^+ + \text{e}^- & \longrightarrow \text{H}
\end{align*}
\]

as given by Kelly(50). Slow adsorption of phosphate ions on the surface accounted for the reduction in corrosion rates for tests conducted 1 hr. after immersion into solution. Other work, not with phosphoric acid but in phosphate solutions, confirm the fact that steel passivates in the presence of phosphate either by the formation of an iron-phosphate film or by plugging up of the pores on ferric oxide films(72-77).

It was seen that the first treatment of weathering steel by phosphoric acid had a retarding effect on the atmospheric corrosion rates. It was also shown that even the earliest surface films consisted of the amorphous iron-oxide-hydroxide films, as opposed to iron-phosphate films that have been reported in the literature(75-77).

Sato and co-workers who proposed the membrane potential system to explain corrosion characteristics(69), had argued that the precipitate film on steel was ferric hydroxide and this film played the role of an anion selective membrane. On their work with the effect of the molybdate anion on ion selectivity in NaCl and KCl solutions, these scientists found that the \(\text{MO}^2-\) species adsorbed to the surface of the precipitate and thus introduced bipolarity
Figure 1.1.11 illustrates the formation of ion selective membranes on precipitate films.

The adsorbed MoO$_4^{2-}$ ions are capable of combining with multivalent cations in solutions. Due to this strong binding force of MoO$_4^{2-}$ ions, the hydrous ferric oxide membrane with adsorbed MoO$_4^{2-}$ ions exhibits cation-selective behaviour in chloride solution containing monovalent cations and anion-selective behaviour in solutions of multivalent cations. This would mean that the adsorption of multivalent cations is sufficiently strong to restrain these cations on the membrane surface, with the fixed charge being reversed from negative to positive. This situation of charge reversal was also observed for nickel chromate, molybdate and tungstate. Sato et al. suggested that this behaviour was common to PO$_4^{4-}$ anions also, which would allow films on weathering steel surfaces to form the favourable bipolarity shown. Thus, on the basis of selective ion flow through the corrosion product layers on steel, the atmospheric corrosion resistance can be expected to be enhanced.

Objectives

It can be seen from the preceding discussion that regarding the initial stages of the dissolution of steel in various media (acidic, neutral or basic), the main steps in the process and the electrochemical parameters that are tests for them are fairly well defined. The same can be said, perhaps to a lesser extent, about the influence of
anions, particularly Cl$^-$ ion on these electrochemical processes in terms of specific adsorption etc. Less can be said about how well the same processes are defined in the presence of oxide and oxide-hydroxide films. The complex effect of film formation on electrochemical parameters makes the electrokinetic mechanisms more difficult to characterize. This is especially true when the films form, as for example on weathering steel under atmospheric corrosion conditions, that can be stoichiometrically not well defined, crystalline to varying degrees, and contain phases that may even be unknown. This is shown in the second part of the study with the results of the field testing. However, in view of the fact that a wealth of information regarding the identity, conditions, and mechanisms of formation of these multitude of phases has been accumulated in this work and others, the following electrochemical studies were proposed:

a) Test the present understanding of the kinetics of dissolution of iron and steel with respect to weathering steel used in atmospheric corrosion.

b) Determine the effect of film formation on the dissolution kinetics and evaluate its consequences with regard to atmospheric corrosion.

c) Follow the bulk concentrations of the dissolution products of iron by an analytical technique and use this information to characterize the reaction path, again to better understand the processes of atmospheric corrosion.
d) Explain the influence of the phosphoric acid inhibitor on weathering steel surfaces on atmospheric corrosion testing, and

e) Use of the same analytical technique for a better elucidation of the corrosion processes, particularly to monitor the formation of films on the surface.
Fig. 1.1.1. Relationship between corrosion rate and the thickness of the moisture film.

Table 1.1.1. Change of free energy (isobaric potential) in transition of metals to the ionic state.
<table>
<thead>
<tr>
<th>Oxidation number</th>
<th>Formula</th>
<th>$\Delta F$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid species</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>Fe</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Fe(OH)$_2$</td>
<td>-118.2</td>
</tr>
<tr>
<td>2.67</td>
<td>Fe$_2$O$_3$</td>
<td>-242.4</td>
</tr>
<tr>
<td>3</td>
<td>FeOH$_2$</td>
<td>-166.0</td>
</tr>
<tr>
<td>3</td>
<td>$\alpha$-FeOOH</td>
<td>-118.6</td>
</tr>
<tr>
<td>3</td>
<td>$\gamma$-FeOOH</td>
<td>-112.5</td>
</tr>
<tr>
<td>Dissolved species</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Fe$^4+$</td>
<td>-20.30</td>
</tr>
<tr>
<td>2</td>
<td>FeOH</td>
<td>-67.80</td>
</tr>
<tr>
<td>2</td>
<td>HFeO$_6$</td>
<td>-92.2</td>
</tr>
<tr>
<td>2</td>
<td>Fe(OH)$_2$</td>
<td>-138.9</td>
</tr>
<tr>
<td>2</td>
<td>FeO$_4^{2-}$</td>
<td>-72.4</td>
</tr>
<tr>
<td>2</td>
<td>Fe(OH)${}^+$</td>
<td>-185.8</td>
</tr>
<tr>
<td>3</td>
<td>Fe$^{3+}$</td>
<td>2.53</td>
</tr>
<tr>
<td>3</td>
<td>FeOH${}^{++}$</td>
<td>-55.96</td>
</tr>
<tr>
<td>3</td>
<td>Fe(OH)$_3$</td>
<td>-106.14</td>
</tr>
<tr>
<td>3</td>
<td>Fe(OH)$_3$</td>
<td>-196.8</td>
</tr>
</tbody>
</table>

Table 1.1.2.

Standard free energies of formation for species of the iron-water system.

Fig. 1.1.2.

Energetical illustration of a materials resistance to corrosion.
Fig. 1.1.3. Potential-pH diagram for iron-water system.

Fig. 1.1.4. A schematic representation of the structure of an electrified interface.
Fig. 1.1.5. The experimentally measured Tafel constant.

Fig. 1.1.6. Dissolution of a Pt electrode.

Fig. 1.1.7. Rates of corrosion of steel, 1) Na$_2$CO$_3$, 2) NaHCO$_3$, 3) NaNO$_3$, 4) NaSO$_4$, 5) NaCl.
Fig. 1.1.8. Dependence of the Cd dissolution rate at constant potential on [KI].

Fig. 1.1.9. Dependence of the desorption rate of I ions at potential $-0.335$ V on the preliminary polarization potential ($-0.174$-I, $-0.124$-II).
Fig. 1.1.10. Schematic representation of the corrosion reaction of iron beneath a precipitate film.

Fig. 1.1.11. Bipolarity of precipitate films.
1.2 EXPERIMENTAL

Potentiostatic and potentiodynamic tests were carried out to determine the various electrochemical parameters for the weathering steels and their mechanisms of corrosion.

a) Potentiostatic Tests

These tests, in which the current response versus time would be monitored at constant potential were carried out using the ECO instruments Model-552 Potentiostat, Model 560 log interface and model 567 function generator in conjunction with a Perkin-Elmer 561 time scale recorder. After determining the rest potential by linear polarization (i.e. slow scan at very small sweep rates), the potentiostatic tests were carried out at these potentials or at potentials slightly negative or positive of the rest potential \( E(rp) \). The starting current values, therefore, were either zero or close to zero except for the tests specifically to measure this effect. During the potentiostatic tests the pH and the \( E(rp) \) were continuously monitored. The \( E(rp) \) was measured at specific intervals by using an inbuilt circuit of the potentiostat that allowed for the compensation of the potential to zero current. De-aerated tests were also carried out with different pH values. The analytical technique used to determine the concentration of iron ions in solution was differential pulse polarography, a short description of which is presented here.
The Differential Pulse Polarographic Technique

The dropping mercury electrode, its various modes of usage, the theoretical basis and the advantages and disadvantages associated with it, etc., have been the subject of many excellent books, review papers and articles (78-83). A comprehensive description need not be given here.

Differential pulse polarography (DPP) is the most sensitive of polarographic techniques and is regarded as a trace analytical technique superior to atomic or molecular absorption spectroscopy and chromatographic approaches for speciation problems. Parry and Osteryoung (84-85) have used the pulse polarographic technique in the analysis of metal ions in solution at very low concentrations e.g., the determination of ferric, ferrous, and cuprous ions in process analysis. Beyer et al. (86) have made simultaneous polarographic measurements of ferrous, ferric, and total iron in standard rocks for purposes of geochemical analysis. Varma (87) demonstrated the use of the technique for corrosion studies on noble metals. He measured concentrations of palladium in a pyridine-hydrochloric acid medium that exhibited extremely small corrosion rates of palladium.

The polarographic half-wave potential of iron in non-complexing media appears at more positive potentials than the oxidation of mercury. In a suitable complexing medium though, in which the complexing ion has a stronger affinity for one of the ionic forms of iron, these concentrations...
trations can be determined rapidly and very accurately. Such a complexing medium is sodium pyrophosphate (Na$_4$P$_{2}$O$_7$) in which the Fe(III)-pyrophosphate reduces at a more negative potential than its ferrous counter-part on the mercury surface. The pH of the supporting electrolyte has to be adjusted to 9.0 for the best results. An example of the simultaneous determination of ferrous and ferric ion concentrations can be seen in figure 1.2.1.

Polarographic Fe(II), Fe(III) determinations were made during the potentiostatic tests removing samples from the corroding solution periodically, (about every twenty to twenty five minutes) and injecting them into the polarographic cell containing the pyrophosphate supporting electrolyte. This electrolyte was purged of air by passing purified argon gas.

The de-aeration of the polarographic cell is an important feature of this important technique and the complicating role dissolved oxygen plays in polarographic measurements needs to be commented on. Dissolved oxygen reduces at the mercury electrode at two stages:

First stage, (potentials v.s. SCE)

\[
\begin{align*}
0 + 2H_2O + 2e^- & \rightarrow H_2O + 2OH^- & E(1/2) = -0.05 \text{ V} \\
2 & 2 & 2 & 2
\end{align*}
\]

Second stage,

\[
\begin{align*}
0 + 2H_2O + 4e^- & \rightarrow 4OH^- & E(1/2) = -0.5 \text{ to } -1.3 \text{ V} \\
2 & 2
\end{align*}
\]

The hydrogen peroxide produced in the first stage can have deleterious effects on the determination of the
electroactive species. The electro-reduction of oxygen also occurs at the vicinity of the mercury electrode dramatically changing the pH. This localized increase in the pH also has adverse effects on the solubility of other species. The complicating influence of the presence of oxygen on polarographic determinations can be seen in figure 1.2.2.

Due to the reasons mentioned above, de-aeration is necessary and in all polarographic measurements the cell was purged with purified argon gas for ten to fifteen minutes prior to the injection of the corrosion solution sample. The purified argon was obtained by the technique described below:

A vanadous chloride solution was prepared by boiling two grams of ammonium metavanadate with 25 mls of concentrated hydrochloric acid and diluting to 250 ml. The solution was next reduced with a few grams of lightly amalgamated zinc. The zinc can be amalgamated by washing in hydrochloric acid solution in the presence of mercury. The blue-green vanadium solution that resulted was reduced to the violet vanadium(II) stage by passing argon gas until a clear violet colour was obtained. This assembly, shown in figure 1.2.3, was then inserted between the polarographic cell and argon tank. When exhausted, as understood by the loss of violet colour, the vanadous chloride solution was regenerated by the addition of a few mls of concentrated hydrochloric acid.
The polarographic analysis was carried out by the EG&G Princeton Applied Research Polarographic Analyzer-Model 383, the PAR Model 303 Static Mercury Drop electrode assembly and chart recorder. All functions of blank subtracting, tangent fit and peak location and concentration determinations were done by the pre-programmed polarographic analyzer after the standards were prepared and calibration curves plotted. The blank was made up of the supporting electrolyte plus an aliquot of the electrolyte solution taken before the specimen was mounted. The supporting electrolyte was replaced with a fresh solution and de-aerated right after the blank run. This procedure was repeated until the end of the potentiostatic test.

**Potentiodynamic tests**

Potentiodynamic tests were run on the ECO instrument described earlier with the logarithmic scale. The output was connected to a Houston Instruments-Omnigraphic X-Y recorder. Different sweep rates, that ranged from 0.1 to 10 mV/s, were used for comparison purposes. The corrosion potentials and corrosion currents as well as the Tafel constants were measured from the polarization curves using the standard procedure.

**Electrochemical cell**

The standard four electrode assembly was used in all tests with two platinum counter electrodes, saturated calomel reference electrode with luggin capillary probe and
the weathering steel as the working electrode. The working electrode was a cube specimen approximately 1\*1\*1 cm, mounted in cold air hardenable resin with only one face exposed to the solution. The working electrode surfaces were prepared using the ASTM standard procedure for electrochemical testing, section G-5(106), grinding with 240 mesh paper and washing with distilled and de-ionised water as well as methyl-alcohol prior to the testing. The solution was gently stirred with a magnetic stirrer throughout the tests. Due to the size of the specimens all currents are in ma/cm$^2$.

Solutions

All solutions were made from reagent grade chemicals using distilled de-ionised water. Because the objective was to better understand the atmospheric corrosion mechanisms of weathering steel, solutions were also prepared to best simulate the conditions in the field. Phosphoric acid solutions were 25% strong, the same concentrations used for the surface treatment of field coupons. Sodium chloride solutions were 0.1%, representative of the field but higher and lower concentrations were also used for comparison purposes, such as 1% and 0.01%. NaN$_3$ solutions that were 3 0.1% were also prepared and used in an attempt to clarify by difference the effects of the specific adsorption of chloride ions.
Materials

Chemical compositions of some weathering steels used in highway bridges are given in Table 1.2.1. Most of the tests used U.S.Steel A588- Grade A but other steels A588 - Grade B and Kawasaki steel A588-Grade A, were also used for comparison.
**FIGURE 3.** Differential pulse polarography of Fe(III)/Fe(II) mixture
0.1 M Na₄P₂O₇, pH 9.0
Scan rate 5 mV/sec, mod. amp 25 V
A = Blank
B = Blank + 25 ppm Fe(III)
C = Blank + 10 ppm Fe(II) and 25 ppm Fe(III)

**Fig. 1.2.1.** The simultaneous determination of ferrous and ferric ions in solution by differential pulse polarography (DPP).
Fig. 1.2.2. Effect of the presence of oxygen.

Fig. 1.2.3. Purifying system for tank argon gas.
<table>
<thead>
<tr>
<th>Type of Steel</th>
<th>Chemical Composition, wt.%</th>
<th>Mechanical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>Si</td>
</tr>
<tr>
<td>Kawasaki Steel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A588-Grade A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Riverton-R</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kawasaki Steel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A325-Type 3-(c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U.S. Steel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A588-Grade A</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.2.1. Chemical compositions of representative weathering steels.
1.3 RESULTS

Potentiostatic Tests

The comparison of the potentiostatic response of a series of weathering steels and a mild steel was made by defining the parameter 'm' as the slope of the current vs. time plots, as demonstrated by figure 1.3.1. The slope m, was determined for conditions of different set potential, pH and electrolyte solution.

This quantity can be conceived to describe the rate of change of the rate of metal dissolution. In Table 1.3.1 is a summary of the results for different grades of weathering steel, the compositions of which were given in the experimental section. Also listed are the open circuit potentials of the different steels upon total immersion into 0.1% NaCl solution of pH 7. All potentials given are vs. \( \text{SCE} \) and all current densities mA/cm based on geometrical area. The experiments were carried out at a potential corresponding to the open circuit potential of each material.

Effect of pH

Table 1.3.2 compares 'm' values for grade A weathering steel and Japanese steels for tests conducted under similar conditions of solution concentration and constant potential[corresponding to E(oc)] but at a pH of 11.5.

The values indicate a reduction of about one or two orders of magnitude for the value of 'm' in basic solutions as compared to neutral.
**Effect of the polarization potential**

The influence of the initial value of the polarization potential, i.e., a comparison of the influence of constant test potentials that are positive or negative with respect to the initial open circuit potential $E_{oc}$, was also investigated. All data are for grade A weathering steel in NaCl solution of pH 7. Applied potentials more noble than $E_{oc}$ produce a negative initial current and potentials less noble than $E_{oc}$ give positive initial currents whose change with respect to time is given by the value of 'm' shown in Table 1.3.3.

**Effect of different anions**

Different anions in solution are aggressive to the steel surface to differing degrees. This effect was demonstrated at pH 7 for grade A steels. The values of 'm' were determined for steel in 0.1% NaNO$_3$ and 0.1% NaCl solutions. Tests were carried out at a value of the constant potential that was the open circuit potential for the steel in each of the solutions. Table 1.3.4 contains the difference in the rate of change of the current for the two solutions as demonstrated by the value of 'm'.

**Stabilization of the rest potential**

The significant electrochemical feature of weathering steel as well as mild steel, pertaining to atmospheric corrosion, is the shift of the rest potential or open circuit corrosion potential towards more noble potentials.
This phenomenon would play an important role in the final products of the atmospheric corrosion process, thus in the protective nature of the corrosion product on weathering steels. This shift, termed the stabilization of the rest potential, is shown in figure 1.3.2 for weathering steels grade A, grade B and a mild steel. All of these show a shift in the rest potential as a function of time, the potential itself stabilizing at a constant value after a period of time. Significant dissolution and film formation take place during the stabilization of the rest potential and the corrosion products formed after stabilization are the oxide-hydroxide forms that are seen in the field testing of weathering steel coupons, discussed in the next section.

The infrared absorption pattern of the corrosion product formed during the stabilization of the rest potential of grade A weathering steel in 0.1% NaCl solution at a constant potential equal to the open circuit potential can be seen in figure 1.3.3.

Whether this shift of the initial rest potential to nobler potentials was due to the specific surface preparation technique of the electrochemical samples prior to the tests was investigated by different surface preparations subsequent to the grinding of the surface. Short dips in 10% solutions of H2SO4 and HCl, both strong acids, were performed with the intention of removing the microscopic thin oxide film that forms on surfaces by air oxidation.
after surface preparation. Figure 1.3.4 compares the current vs. time profiles of etched and un-etched A588 steel grade A samples, with the extent of the change of the rest potential for each test also given.

Specific adsorption effects

The influence of different electrolyte anions was further investigated by comparing the current vs. time curves for potentiostatic tests for NaCl and NaNO₃ solutions of similar strength. The nitrate anion is known to have a much smaller affinity for adsorption on the steel surface than the chloride. Figures 1.3.5-6 are current vs. time curves for these two electrolytes in the presence and absence of oxygen. The rest potentials (Eₑ), their extent of change (Δ Eₑ) and the value of the constant test potential (Eₚ) also are shown on the figures.

Polarographic tests, bare steel

A series of tests were made measuring the following four parameters with respect to time simultaneously during the same test: current (i), pH, rest potential (Eₑ) and, by use of polarography, the bulk electrolyte concentration ratio [Fe(II)]/[Fe(III)]. This ratio was determined as a function of time as described in the experimental section. The polarographic plots of the current of reduction for the Fe(II) and Fe(III) complexes on the surface of the mercury vs. the scan potential for the simultaneous measurements can
be seen in figures 1.3.7-10. A calibration plot of the standards and a summary of the method programmed into the polarographic analyzer with all the settings are shown in figure 1.3.11.

The results of the tests for a bare weathering steel sample in an unpurged 0.1% NaCl solution in which all the four parameters were measured are presented in figure 1.3.12. Similar plots for a purged solution of 0.1% NaCl are shown on figure 1.3.13. Purging was done by purified argon gas and continued for approximately one hour until the pH of the solution stabilized. The corrosion products from these tests were dried, pelletized in KBr and analysed by infrared spectroscopy for phase identification. The IR patterns are illustrated seen in figure 1.3.14.

**Inhibition effects by phosphoric acid**

Phosphoric acid is widely used as an inhibitor for steel in cooling water treatment in neutral environments and other industrial applications, as mentioned in the Introduction. Phosphoric acid can be used either by addition into aqueous media or by surface application by spraying or spreading, as in atmospheric corrosion inhibition described in Part 2.

Potentiostatic tests were performed to simulate the conditions in the field of weathering steel surfaces treated by phosphoric acid prior to exposure in the atmosphere. The electrochemical samples, after standard surface
preparation, were treated with 25% phosphoric acid and left to dry for one whole day before potentiostatic tests and polarographic determinations were made. For the latter parameters; $i$, $E$, pH and $[\text{Fe(II)}]/[\text{Fe(III)}]$ were measured with respect to time. Figures 1.3.15-16 show the results for argon purged and un-purged solutions of 0.1% NaCl.

Figures 1.3.17-18 illustrate the same measurements for weathering steel samples in 25% phosphoric acid. $[\text{Fe(II)}]/[\text{Fe(III)}]$ ratios could not be determined for phosphoric acid solutions due to the dramatic changes it produced in the pH of the polarographic cell and the complexities introduced by this factor into the reduction potentials of the Fe(II) and Fe(III) complexes in the pyrophosphate supporting electrolyte.

Potentiodynamic tests

Potentiodynamic tests were made to determine the cathodic and anodic polarization curves. These curves then were used to measure Tafel constants, corrosion potentials and corrosion currents that could be used to calculate corrosion rates pertaining to the accelerated testing conditions of the electrochemical test. Next, these results could be compared with corrosion rates from field testing of weathering steel under atmospheric exposure conditions.

As described in the Introduction, the Tafel constants are used to test the various mechanisms that explain the initial stages of the dissolution of iron in aqueous
solutions.

Figures 1.3.19-20 show the E v.s. i behaviour of bare weathering steel grade A, in solutions of 0.1% NaCl, 1% NaCl and 0.1% NaNO₃ at different potentiodynamic scan rates. The determination of Tafel constants are also shown. The various constants, corrosion currents and potentials are summarized in Table 1.3.5.

Potentiodynamic characterization of inhibited surfaces was demonstrated for both phosphoric acid solutions and phosphoric acid surface treatments. Tafel constants, corrosion currents and potentials as well as the passivation potential of weathering steel in phosphoric acid solutions were all measured. Figures 1.3.21-24 show the anodic and cathodic polarization curves and Table 1.3.6 summarizes the different parameters.
Fig. 1.3.1. The definition of 'm', the slope of the \( i \) v.s. \( t \) curve.

\[
\frac{\Delta i}{\Delta t} = M \frac{mA}{min}
\]

<table>
<thead>
<tr>
<th>steel</th>
<th>grade A</th>
<th>grade B</th>
<th>japanese steel</th>
<th>mild steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m(\text{mA/min}) )</td>
<td>0.06</td>
<td>0.035</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>( E (\text{mV}) )</td>
<td>-440</td>
<td>-464</td>
<td>-445</td>
<td>-350</td>
</tr>
<tr>
<td>( E_{oc} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

where \( E_{oc} \) = open circuit potential

Table 1.3.1. Comparison of different weathering steels in terms 'm' and the open circuit potential.

<table>
<thead>
<tr>
<th>steel</th>
<th>grade A</th>
<th>japanese steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m )</td>
<td>0.00072</td>
<td>0.0018</td>
</tr>
</tbody>
</table>

Table 1.3.2. Effect of pH 11.5 on 'm' for Grade A and Japanese steel.
Table 1.3.3. Effect of set potential on the value of 'm'.
Grade A steel, 0.1% NaCl.

<table>
<thead>
<tr>
<th>SET POTENTIAL</th>
<th>m</th>
<th>LOG m</th>
</tr>
</thead>
<tbody>
<tr>
<td>-550</td>
<td>0.00015</td>
<td>-3.80</td>
</tr>
<tr>
<td>-500</td>
<td>0.0045</td>
<td>-2.35</td>
</tr>
<tr>
<td>-475</td>
<td>0.010</td>
<td>-2.00</td>
</tr>
<tr>
<td>-450</td>
<td>0.075</td>
<td>-1.12</td>
</tr>
<tr>
<td>-440</td>
<td>0.06</td>
<td>-1.20</td>
</tr>
<tr>
<td>-420</td>
<td>0.3</td>
<td>-0.52</td>
</tr>
<tr>
<td>-380</td>
<td>2.34</td>
<td>0.37</td>
</tr>
<tr>
<td>-340</td>
<td>11.7</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 1.3.4. Effect solution anion on 'm', grade A steel.

<table>
<thead>
<tr>
<th>solution</th>
<th>0.1% NaCl</th>
<th>0.1% NaN03</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>0.06</td>
<td>0.001</td>
</tr>
</tbody>
</table>


Stabilization of rest potentials, a) grade A steel, b) grade B steel c) mild steel. Fig. 1.3.2.
Fig. 1.3.3. Infrared pattern of corrosion product from potentiostatic test, grade A steel, 0.1% NaCl.
Fig. 1.3.4. Effect of prior surface treatment on the i vs. t profiles of grade A weathering steel in 0.1% NaCl.

- □ un-etched, purged. △E = -225 mV
- + 10% H2SO4 etch. △E = -220 mV
- △ 10% HCl etch. △E = -215 mV
Fig. 1.3.5. Effect of specific adsorption of chloride, grade A
- 0.1% NaCl unpurged, $E(\text{rp}) = -440$, $E(\text{set}) = -400$, $\Delta E = 220$
+ 0.1% NaNO unpurged, $E(\text{rp}) = -350$, $E(\text{set}) = -300$, $\Delta E = 35$
Specific adsorption of chloride and the variation of pH, grade A steel.

Δ 0.1% NaCl-purged. E(rp) = -510, E(set) = -400, ΔE = 130
+ 0.1% NaNO₃-purged. E(rp) = -470, E(set) = -400, ΔE = 20
Fig. 1.3.7.

Polarographic analysis of potentiostatic test with grade A steel in 0.1% NaCl- unpurged. Bold numbers indicating sampling time in minutes.
Fig. 1.3.7.

Polarographic analysis of potentiostatic test with grade A steel in 0.1% NaCl- unpurged. Bold numbers indicating sampling time in minutes.
Polarographic analysis of potentiostatic test with grade A steel in 0.1% NaCl-purged.

Fig. 1.3.8.
Fig. 1.3.8.

Polarographic analysis of potentiostatic test with grade A steel in 0.1% NaCl-purged.
Fig. 1.3.9.

Polarographic analysis; phosphoric acid treated sample, unpurged.
Fig. 1.3.10. Polarographic analysis, phosphoric acid treated sample, purged.
Fig. 1.3.10. Polarographic analysis, phosphoric acid treated sample, purged.
Fig. 1.3.11. Method of analysis and calibration plot for polarographic analysis.
Fig. 1.3.12. Simultaneous determination of i, E(rp), pH and the ratio Fe(II)/Fe(III) for bare steel in 0.1% NaCl.
Simultaneous determination of the four parameters for bare steel in purged 0.1% NaCl.
Fig. 1.3.14. Infrared patterns of the corrosion products from potentiostatic tests with bare grade A steel: a) purged, b) unpurged solution of 0.1% NaCl.
Simultaneous determination of the four parameters for phosphoric acid treated samples in 0.1% NaCl.
Simultaneous determination of the four parameters in purged 0.1% NaCl solution phosphoric acid trt.
Fig. 1.3.17. Unpurged 25% phosphoric acid solution.
Fig. 1.3.18. Purged 25% phosphoric acid solution.
Fig. 1.3.19. E v.s. i plot for bare grade A steel in 0.1% NaCl. Sweep rates a)0.1 mV/s b)1mV/s.
Fig. 1.3.20. E v.s. i plot for bare grade A steel in 1% NaCl. Sweep rates a)0.1mV/s b)1mV/s.
Table 1.3.5. Electrochemical parameters at different sweep rates for grade A steel in 0.1% NaCl, 1% NaCl.

<table>
<thead>
<tr>
<th>Sweep Rate (mV/s)</th>
<th>b(anodic) (mV/dec)</th>
<th>b(cathodic) (mV/dec)</th>
<th>E(corr) (mV)</th>
<th>i(corr) (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>55</td>
<td>130</td>
<td>-390</td>
<td>0.26</td>
</tr>
<tr>
<td>1.0</td>
<td>60</td>
<td>135</td>
<td>-385</td>
<td>0.19</td>
</tr>
<tr>
<td>Grade A steel, 1% NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>63</td>
<td>140</td>
<td>-448</td>
<td>0.20</td>
</tr>
<tr>
<td>1.0</td>
<td>56</td>
<td>145</td>
<td>-440</td>
<td>0.155</td>
</tr>
<tr>
<td>Grade A steel, 0.1% NaNO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>58</td>
<td>115</td>
<td>-325</td>
<td>0.145</td>
</tr>
</tbody>
</table>
Fig. 1.3.21. E vs. i plot for phosphoric acid treated sample in 0.1% NaCl, sweep rate 0.1 mV/s.
Fig. 1.3.22. E v.s. i plot for phosphoric acid treated sample in 0.1% NaCl, sweep rate 1 mV/s.
Fig. 1.3.23.
E v.s. i plot for sample in phosphoric acid solution, sweep rate 0.1 mV/s.

Fig. 1.3.24.
E v.s. i plot for sample in phosphoric acid solution, sweep rate 1 mV/s.
Phosphoric Acid Surface Treatment (25%)  
Grade A steel, 0.1% NaCl

<table>
<thead>
<tr>
<th>sweep rate</th>
<th>b(anodic)</th>
<th>b(cathodic)</th>
<th>E(corr)</th>
<th>i(corr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>70</td>
<td>120</td>
<td>-435</td>
<td>0.125</td>
</tr>
<tr>
<td>1.0</td>
<td>75</td>
<td>130</td>
<td>-460</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Phosphoric Acid Solution (25%)  
Grade A steel

<table>
<thead>
<tr>
<th>sweep rate</th>
<th>b(anodic)</th>
<th>b(cathodic)</th>
<th>E(corr)</th>
<th>i(corr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>42</td>
<td>125</td>
<td>-395</td>
<td>1.2</td>
</tr>
<tr>
<td>1.0</td>
<td>37</td>
<td>130</td>
<td>-420</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Table 1.3.6. Electrochemical parameters at different sweep rates for phosphoric acid treated samples and in phosphoric acid solutions.
1.4 DISCUSSION

The results of potentiostatic tests performed on the weathering steels simulating atmospheric corrosion conditions clearly indicated that the corrosion process can be divided into two distinct parts with completely different kinetic laws governing them. These are the dissolution of the steel prior to the formation of the insoluble corrosion product layer and corrosion processes that follow thereafter. All measured parameters reach more or less steady-state values, determined no doubt by the nature of the corrosion product formed on the steel surface. The compactness, electrical nature, adherence and compatibility of the film with the steel surface will all be influential during this latter stage of corrosion.

The fact that these constant potential tests are successfully able to reproduce the processes occurring under thin electrolyte layers in the atmosphere is evidenced by the corrosion products formed. These are the same oxide-hydroxides and amorphous rusts that are found in the atmospheric exposure testing of weathering steel. In addition, there is evidence from corrosion rate measurements from exposure tests that the above mentioned steady-state conditions are established there also. Figure 1.4.1 illustrates weight loss values that demonstrate this trend. The most significant difference between laboratory potentiostatic tests and atmospheric tests lies in the time span involved
in the attainment of steady state conditions. Atmospheric corrosion proceeds at a much slower rate, the importance of which will be discussed later.

The results for the uninhibited system will be discussed separately in terms of these two analogies. Likewise, for the phosphoric acid inhibited surfaces the results will be discussed under a separate heading.

1.4.1 Dissolution of weathering steel in neutral chloride environments

Two observations are significant when a weathering steel specimen is immersed into an aqueous solution that contains chloride ions - the constancy of the current - time profile and the large negative shift in the open circuit potential of the material. The current - time curve, shown schematically in figure 1.3.1, was used to define the slope(m) in mA/min. This parameter, a measure of the rate of change of the dissolution rate was determined for different types of weathering steel and a mild steel(Table 1.3.1). The tests were done at the open circuit potential of each steel, also indicated in the Table. The open circuit potential of the steel, E(oc), is defined as the potential at which the current measured is nil upon initial immersion into the solution, as opposed to the rest potential, E(rp), which is the value of the potential corresponding to zero current measured at different points in the experiment. It is the rest potential that shifts towards
more noble values from an initial value equal to the open circuit potential.

The m values for different steels are seen to be fairly close, ranging from 0.035 to 0.06 mA/min, compared to those obtained in more basic solution. Table 1.3.2 contains values of m which are greatly reduced (~ 0.001) from those in Table 1.3.1, for a solution of pH 11.5 and A588 grade A US steel and Kawasaki steels.

The large negative shift in the rest potential of the steel and its stabilization at a particular value is peculiar to chloride solutions. This is shown in figure 1.3.2 for two weathering steels and a mild steel. The shift of about 200 mV is quite significant and it takes different amounts of time for stabilization to set in for different steels. Small shifts in open circuit potential after immersion into solution are quite common in electrochemical testing, with shifts of about 10 mV around the initial rest potential in the course of several hours(88). Akimov(24) measured potential shifts for several metals and reported a value of about 150 mV for iron in 3% NaCl solution. Purins and Liepina also observed an effect of about the same magnitude for iron in NaCl and KCl solutions(90). Apart from the equilibration of the corrosion potential when immersed into the solution, the much larger negative shift in the rest potential is often accompanied by intensive attack on the steel surface. This was observed by Akimov
for copper in chloride containing nitric acid solution. As mentioned earlier in the Introduction, Kolotyrkin stated that solution anions, and particularly chloride, participate directly in the elementary act of the ionization of the metal(58). Kolotyrkin envisaged the formation of species such as Fe(Cl) and it seems likely, especially in view of the observations made by Foley(89), that species of the form (FeClOH) inevitably form and determine the nature of the corrosion process. These metal-anion complexes are mostly transitory, sometimes stable and insoluble, but always an essential part of the dissolution process. The initial adsorption of chloride ions on the electrode surface is largely determined by a quantity known as the potential of zero charge, \( E(zc) \). Frumkin defined this as the metal potential measured against a reference electrode under conditions of zero charge on the metal(23). At the \( E(zc) \), the electrical double layer is absent at the electrode with the absence of specific ion adsorption, and it can be seen that the charge on an electrode in a particular solution will be determined by the position of the equilibrium potential of the metal in that solution with respect to the \( E(zc) \). The potential of zero charge for iron has been reported to be between \(-0.4\) V and \(-0.8\) V vs. SHE, demonstrating the different values obtained by different workers using different methods(57). The chloride ion will strongly adsorb on the steel surface when it is positively charged or when its
equilibrium potential in a solution is more positive than the \( E(zc) \). Once the chloride ion adsorbs on the surface due to its high capacity for adsorption and low polarizability of its electron shells, it has a direct effect on the electrochemical reactions.

Additional evidence for the formation of metal-chloride complexes that influence the kinetics of corrosion reactions was provided by the results of the tests done to compare the effect of different solution anions on the kinetics. The nitrate ion is known to be considerably less aggressive towards the steel surface than chloride. In Table 1.3.4 is a comparison of \( m \) values for solutions of NaCl and NaNO\(_3\) of similar strength. An order of magnitude lower value for the nitrate solution points out to the relatively low ability of the nitrate ion to adsorb on the steel surface and subsequently form the metal-nitrate complexes. These complexes would play the role of carrying the ferrous ion into the solution due to their higher stabilities. This naturally results in lower reaction rates, indicated by the slope of the \( i \) vs. \( t \) curve. Figures 1.3.5 and 1.3.6 also show this effect dramatically influencing the level to which the current rises and more significantly the absence of any major shift in the rest potential for the nitrate solution. The effect of dissolved oxygen also would seem to be secondary in the presence of aggressive solution anions. In purged solutions containing no dissolved oxygen-
(figure 1.3.6), the only difference would seem to be the relative speed with which the rest potential and current stabilize compared to the aerated solution. In aerated solution currents stabilized after 20 and 120 minutes for NaCl and NaNO solutions respectively, whereas in purged solution this time was approximately 5 minutes for both solutions. The initial polarization potential also has a major effect on the value of m and thus the time taken to stabilization. Table 1.3.3 lists the effect of the position of the set potential, $E_{\text{set}}$, on the value of m, and the rate at which the reaction will proceed to steady-state. The greater the displacement of the constant set potential from the open circuit potential in the positive direction, the greater the rate of reaction. The values in Table 1.3.3 were plotted as displacement from the open circuit potential vs. log m and are shown in figure 1.4.2. The values fit a straight line plot and suggest a linear dependence of log m on the extent of specific adsorption of chloride that is determined by the potential displacement. Displacements much greater than 100 mV in the positive direction could not be carried out due to the speed with which the sample would corrode and make observations on the uniform, filmless part of the process impossible. However this effect, observed also by Kolotyrkin and co-workers (91-92) is important in that it confirms the influence of the initial polarization potential on the chloride ion adsorption on the surface of
the electrode. The chemico-adsorptive interaction between chloride ions and the surface atoms of steel takes place at more negative potentials than those corresponding to the corrosion potential. Since the catalytic influence of the chloride on iron dissolution increases with greater displacement in the positive (or less noble) direction it can be concluded that both the strength of the bonds between the adsorbed ion and the surface atoms of steel as well as surface coverage by the chloride ions must be increasing.

This hypothesis was tested by observing the same parameter for increasingly stronger chloride solutions, the results of which are presented in Table 1.4.1 and figure 1.4.3. The value of \( m \), when it reaches around 500 remains constant thereafter. This result also appears on the log \( m \) vs. \%NaCl plot which stabilizes around log \( m = 2.7 \). This is indicative of the rising surface coverage as the chloride concentration is increased and saturation coverage after 5\% salt concentration is reached.

Large negative shifts in rest potentials were observed also for pre-passivated surfaces. Akimov observed that when stainless steel was pre-passivated at about 0.65 V SHE, in a weak solution of KMnO\(_4\), and then immersed into a 3\% salt solution, the electrode potential changed gradually over about 20 hours to a significantly more negative value. This result would seem to be quite similar to the stabilization of the rest potential tests whose results have been
presented. Similar observations on steels in chloride solutions (59,93), led to explanations of the potential shift solely in terms of the destruction of the oxide film on steels as chloride ions gradually penetrate the thickness of the film, lowering the electrode potential in the process.

Whether or not a micro-passive protective film was responsible for the shift in the rest potential was also examined. A thin film could form by air oxidation immediately following the preparation of the surface by grinding and washing. Concentrated sulphuric acid was used to etch the sample for a very brief period of time, then thoroughly washed off before the test was conducted. Etching by concentrated HCl was also tried to preclude the possibility of the formation of any iron sulphate films in the sulphuric acid etch test which might influence the dissolution kinetics. These short dips into strong acid solutions were intended to remove any thin micro-passive layer that would have been formed by air oxidation. This layer could then be gradually penetrated by chloride in solution, perhaps causing the negative shift in the rest potential. Figure 1.3.4 shows the results of these etched-tests compared to the un-etched with the shift in potential for each test noted on the figure. All tests show a shift around 220 mV in the negative direction clearly ruling out the possibility of a protective film being responsible for the shift in the potential. The differences in the time to stabilization
could be due to surface topographic effect as a result of the short etch.

It thus becomes plausible to look at these phenomena in terms of the 'metastable' or 'transient' chloro complexes of iron that are formed by the reaction of solution chloride ions with surface atoms of steel. These complexes then remain relatively stable compared to the individual ferrous ions resulting in the reduction of electrode potential. The fact that the rate of the process increases with greater abundance of chloride ions is then expected. However, one should note that several different events are occurring at the same time. The thermodynamic instability of the steel surface releasing ferrous ions into the solution, the formation of complexes due to the great affinity of chloride ion towards the surface and the subsequent hydrolysis of these complexes by replacement of chloride by hydroxide, all take place concurrently. This replacement, in turn, results in the formation of the oxide-hydroxide films identified on the surface that gradually cover the whole surface and govern the kinetics of the subsequent corrosion processes.

The extreme uniformity of both the rest potential vs. time and current vs. time profiles suggest the operation of a simple, consistent reaction mechanism for the anodic dissolution of steel, until the beginnings of the formation of oxide-hydroxide films.
Dissolution Mechanism

Mechanistic studies that have examined the rate determining step, reaction orders and types pertaining to the dissolution of iron in terms of the Tafel slopes, etc., were given in the Introduction. The results of potentiodynamic tests for Tafel slope determinations are presented in Table 1.3.5 and figures 1.3.19-20 for bare weathering steel grade A in different electrolytes. The anodic Tafel constants, of between 55 and 63 mV agree well with literature values around 60 mV (refer to Introduction). The following reaction sequence and rate determining step formulated by Nobe et al. (62,63) for neutral and alkaline solutions and McCafferty and Hackerman in acidic solutions apply:

\[ \text{Fe} + \text{H}_2\text{O} = \text{Fe}(\text{OH})\text{ads} + \text{e}^- \]
\[ \text{Fe}(\text{OH})\text{ads} + \text{Cl}^- = [\text{FeClOH}]\text{ads} + \text{H}^+ + \text{e}^- \]
\[ [\text{FeClOH}]\text{ads} \rightarrow \text{FeClOH} + \text{e}^- \]
\[ \text{FeClOH} + \text{H} = \text{Fe} + \text{Cl} + \text{H}_2\text{O} \]

or, a sequence similar to the Bockris dissolution mechanism initially (28):

\[ \text{Fe} + \text{OH}^- = \text{Fe(OH)}\text{ads} + \text{e}^- \]
\[ \text{Fe(OH)}\text{ads} \rightarrow \text{Fe(OH)} + \text{e}^- + 2\text{H}^+ \]
\[ \text{Fe(OH)} = \text{Fe} + \text{OH}^- \]

and complexation by:

\[ \text{Fe} + m\text{OH}^- + n\text{Cl}^- \rightarrow [\text{Fe(OH)}_m\text{(Cl)}_n] \]

the overall reaction being
Fe + mOH + nCl \rightarrow FeX + 2e

FeX representing the chloro complex.

In the light of the studies on the effect of chloride concentration on the dissolution rate, it would seem more likely that a mechanism that allows for the direct adsorptive interaction of the chloride with the steel surface is operating. Both these mechanisms unfortunately give similar anodic Tafel slopes around 60 mV (62-64). This was reported also by Turnbull and Gardner for steel in 3.5% NaCl solution (67).

Although the pH was monitored in these tests, it did not vary to a great extent, showing only a slight rise of about 0.5 to 1.0 pH units. The measured pH, however, is the bulk pH and gives little, if any, indication of the conditions in the immediate vicinity of the electrode. The slight rise of pH in air containing solutions could be due to the air oxidation of ferrous to ferric by the following reaction;

\[
\text{4Fe}^{2+} + \text{O}_2 + \text{4H}^+ \rightarrow \text{4Fe}^{3+} + 2\text{H}_2\text{O}
\]

that consumes H\(^+\) ion.

The interesting feature of the results listed in Table 1.3.5 is the fact that different solution concentrations demonstrate similar values indicating that the mechanisms of dissolution are probably the same.

The importance of the negative shift in the rest potential that accompanies the dissolution and film forma-
tion processes no doubt plays an important part in the atmospheric corrosion of these materials. This is borne out by the similarity of corrosion products from both conditions of testing. The precise nature, stability, stoichiometry, and reactivity of the iron-chloro complexes are difficult to determine, as mentioned earlier but spectrochemical techniques that can be applied to this problem are available and such information seems to be needed for an accurate characterization of the elementary dissolution mechanisms in chloride media.

Also included in Table 1.3.5 are the corrosion currents and corrosion potentials for bare weathering steel in chloride solution, calculated by the Tafel extrapolation method demonstrated on figures 1.3.22-23. These results can be used to calculate corrosion rates in terms of weight loss or thickness loss, more commonly in mils per year (mpy), using the following relationship;

\[
\text{corrosion rate (mpy)} = 0.13 \times i(\text{corr}) \times (E.W)/d
\]

where

\[
i(\text{corr}) = \text{corrosion current density, a/cm}^2
\]

\[
E.W. = \text{equivalent weight of corroding species (M/n)}
\]

\[
M = \text{atomic weight}
\]

\[
n = \text{no. of electrons involved in the reaction}
\]

\[
d = \text{density of the corroding species, g/cc}
\]

Using \(d = 7.8 \text{ g/cc}, E.W. = 28 \text{ g}\) and the values of \(i(\text{corr})\) in Table 1.3.5, Table 1.4.2 was assembled giving the weight
loss values for laboratory accelerated tests. This Table also includes some results from atmospheric exposure testing for comparison.

The results indicate that accelerated laboratory testing using salt fog atmosphere and electrochemical techniques, give greater corrosion rates. Immersion testing and rain simulated wet-dry cycling tests give results close to actual values in atmospheric testing. The rather slow rates in atmospheric testing are due to wet-dry cycling and film formation. Longer times also mean more compact and adherent scales with not too much porosity. Also they contain less water due to the drying effect. These factors would all act to reduce corrosion rates. One also has to consider the fact that compared to the duration of exposure testing, corrosion in the presence of the film covers a greater portion of the testing period. On the other hand, the active filmless period in potentiodynamic testing has greater weight proportionally in the corrosion rate.

1.4.2 Dissolution and film formation on weathering steel in chloride solution

As oxide-hydroxide films start growing on the weathering steel surface, the various parameters measured start exhibiting a less active character. The steady rise in the current and the steady fall in the rest potential give way to a stabilization indicated by the lowering of slopes and the reaching of steady state conditions control-
led by the nature of the corrosion product formed. This best can be seen by observing the simultaneously measured parameters, i, E(rp), pH and [Fe(II)]/[Fe(III)]. Figure 1.3.12 shows these results plotted on the same time scale for weathering steel grade A in unpurged 0.1% NaCl. It is striking that all measured parameters show the above mentioned property. In other words, a certain stabilization occurs at about the same time in the potentiostatic test, approximately 200 minutes. Visual observation of the experiment clearly indicates that this stabilization is associated with the precipitation of the insoluble corrosion product film that has an orange/brown colour. This product was confirmed by infrared spectroscopy to be lepidocrocite. The ir pattern can be seen in figure 1.3.14(for standard spectra, refer to part 2).

The absence of oxygen does not seem to make a significant difference in the profiles, except that the potential shift comes to about half the value for that of the unpurged solution (100 mV as opposed to 200 mV). The current values reached at the end of the tests are also lower for the purged solution (figure 1.3.13). The presence of oxygen, however, appears to be significant in determining the ratio [Fe(II)]/[Fe(III)]. Much slower corrosion rates produce less dissolution of the steel, hence a smaller amount of ferrous ions in the solution. Due to the absence of air in the solution, the reaction Fe(II) -----> Fe(III)
does not take place and the ratio increases to the point where the dominantly ferrous oxide-hydroxide amorphous phase starts precipitating. The precipitation corresponds to the time at which the current and rest potential are stabilizing (~300 minutes). The amorphous product was identified by infrared spectroscopy and is shown in figure 1.3.14, together with the corrosion product from the unpurged solution. The ferrous - ferric ratio in the absence of air is determined solely by the variations in the concentration of the ferrous ion. It would seem, however, that a finite amount of ferric ion exists in the solution due perhaps to the fact that persistent purging by argon gas did remove all traces of dissolved air.

Although infrared spectroscopy does not reveal more than one phase, there is evidence from laboratory immersion testing and field exposure testing(146,153), that the oxide-hydroxide film corroding under thin electrolyte in the atmosphere may be of dual nature. Above mentioned observations show that the corrosion product consists of a more compact, non-porous, perhaps amorphous film next to the steel surface and a porous not so compact seemingly more crystalline layer on top of it next to the electrolyte. The corrosion products observed by infrared spectroscopy are representative of a more compact and protective inner layer that does not include great amounts of water. The experience with long durations of atmospheric exposure testing has
shown that the porous non-compact outer layer contains higher concentrations of water and undergoes a series of phase transformations and crystallization in the course of the dry cycles.

Sato and co-workers\(^{(69)}\) envisaged a similar configuration for films formed on steel exposed to the atmosphere, as explained in detail in the Introduction. Sato indicates that in the active or passive state, precipitate films form on steel that are ion selective in character. He suggests that the anodic current in the anion selective films would be carried by anions by migration from the film/solution interface to the metal surface, through a membrane system such as the following:

\[
\begin{array}{c|c|c}
(I) & \text{precipitate} & \text{membrane} \\
\hline
+ & \text{H, OH} & + \\
- & n^+ & n^+ \\
\hline
\text{Fe}^+ & \text{Cl} & \text{Fe}^+ & \text{Cl}
\end{array}
\]

where I and II represent interior phase and bulk solution respectively.

There would be a membrane potential established across the precipitate film that would be equal to,

\[
E_d = -\frac{RT}{F} \ln \left( \frac{a_{\text{Cl}^-}^{\text{II}}}{a_{\text{Cl}^-}^{\text{I}}} \right)
\]

(10)

In view of the fact that two separate films are formed on the surface with different properties, it is plausible to think of the precipitate membrane also composed
of two parts: a) that corresponding to the compact scale, adherent on the surface of the steel and not permeable to chloride ion diffusion from the solution side. A one way traffic of ferrous ions diffusing from the metal surface to the interface of the compact film and the porous layer would determine charge transfer in this film. b) The non-compact, porous layer which transports—with the aid of large amounts of water in the pores—chloride ions from the bulk solution to the compact rust. The situation is drawn schematically in figure 1.1.10.

The metal / compact deposit interface would be severely depleted in solution active species and film growth would take place at the interface of the two layers.

Evans (94) suggested that an electronic process could be responsible for metallic ions entering at the base as an equal number escape from the outer interface to combine with solution anions.

The membrane or diffusion potential acts to push the electrode potential in the noble (negative) direction. That is, an electrode potential measured in the presence of a precipitate film includes the diffusion potential across the film. Due to the difficulty in obtaining accurate values for the concentrations of various species in the complicated system of a corroding metal with corrosion product precipitates on it, it is extremely difficult to derive quantitative models that fit experimental data well. Howe-
ver, by modifying Sato's expression for the diffusion potential, \( E(d) \), to include a double precipitate film structure, i.e.,

\[
E(d) = E(d)_1 + E(d)_2
\]

where 1 and 2 stand for the precipitate films and rearranging, one gets,

\[
E(d) = -\frac{RT}{F} \ln \frac{(a^{2+}_{Fe^2+})_I (a^{Cl^-}_{Cl^-})_I}{(a^{2+}_{Fe^2+})_II (a^{Cl^-}_{Cl^-})_II}
\]

Making some assumptions for the concentrations of the species at the two interfaces, one can calculate a diffusion potential and compare it with experimental values of the total shift in the rest potential. In such a double membrane system, taking the concentration gradient in the region II to region I direction, the interface region would be region I for both membranes. Assuming that there are equal numbers of both species there at any one time for complex formation, i.e. ferrous ions taken up subsequent to their emergence from the compact layer, the expression for the diffusion potential would become;

\[
E(d) = -\frac{RT}{F} \ln \frac{(a^{Cl^-}_{Cl^-})_I}{(a^{Fe^2+}_{Fe^2+})_II}
\]

the term \( (a^{Cl^-}_{Cl^-})_I \) in the bulk can be taken equal to the strength of the solution which is 0.02 M. There is no way of accurately knowing the ferrous ion concentration at the base metal / compact film interface but one can assume that
the measured bulk concentrations prior to film formation at the beginnings of the potentiostatic test gives a reasonable estimate. Taking this value to be about 0.001 M from polarographic measurements, the diffusion potential would calculate to be around -80 mV. This would be the amount with which the electrode potential would have to shift in order to take account of the diffusion potential across the precipitate film. It can be seen that the magnitude calculated using the membrane potential model is in the range of rest potential shifts for most of the potentiostatic tests. A better correlation is not to be expected given the accuracy to which the concentrations of the ionic species can be assumed.

It is not unlikely however, that the ferrous ion emergence from the base metal proceeds at much lower rates than those observed for the more active part of the potentiostatic test when the current vs. time curve has a constant steep slope. Given this, an order of magnitude lower concentration for the ferrous ion would yield a shift of -138 mV. An even lower (two orders of magnitude) concentration would result in a potential shift of up to -198 mV.

It is known that the adsorption of solution anions on the surface of mercury changes the structure of the ionic part of the electronic double layer. Frumkin showed that this adsorption could shift the potential of zero charge in the negative direction (23) in the case of I ion adsorption...
on mercury which is essentially reversible. It is generally accepted that such a shift occurs for the iron electrode as well but whether the adsorption is reversible or not is contested. So conceivably some of the potential shift in the rest potential could be due to specific adsorption and/or complex formation. It is not possible at this stage to separate the potential into its respective parts assigned to the above mentioned effects. This would be achieved by a better knowledge of the nature of the chloro complexes and the concentrations of the various species in the immediate vicinity of the interfaces.

1.4.3 Dissolution and film formation in an inhibited system

Two different types of inhibitor application, namely the surface treatment of the steel by 25% phosphoric acid and immersion into phosphoric acid solution were carried out. The former was an attempt to simulate atmospheric exposure testing of weathering steel in the surface treated condition and the latter to compare the behaviour of steel in a solution of the surface treatment. These two tests, as expected, gave completely different results with respect to their electrochemical behaviour in potentiostatic and potentiodynamic tests.
Inhibition and passivation of weathering steel in phosphoric acid solution.

The passivation of iron and steel in phosphoric acid solutions, or in acidic solutions of phosphates, is well known (72-77, 95, 102). This was demonstrated also by the results of potentiodynamic tests shown in figures 1.3.23 and 24. The passivation potential of grade A weathering steel can be seen to be around -150 mV in 25% phosphoric acid. The presence of oxygen makes little difference in the dissolution kinetics of steel in phosphoric acid, presumably due to the fact that the cathodic reaction is essentially hydrogen evolution at this solution pH. A cathodic Tafel slope of about 120 mV (Table 1.3.6) is reported in literature (71-75), and accounts for the reaction,

\[ +H + e = 1/2 H_2 \]

The anodic dissolution of iron in acidic solutions is also well established (see the review of literature in the Introduction). The Bockris mechanism predicts an anodic Tafel slope of 40 mV which is observed experimentally. The compatibility of the dissolution mechanism of iron in phosphoric acid to that in other acids was confirmed by Rajagopalan et al. (71), who obtained an anodic Tafel slope of about 50 mV. In the Bockris mechanism iron corrodes with the following reactions;

\[ \text{Fe} + \text{H}_2\text{O} = (\text{FeOH})_{\text{ads}} + \text{H}^+ + e^- \]

\[ (\text{FeOH})_{\text{ads}} \rightarrow (\text{FeOH}) + e^- \ RDS \]
Potentiostatic tests in phosphoric acid solution exhibit no negative shift of the rest potential. Figures 1.3.17 and 18 show, especially for the aerated solution, a small shift in the positive direction (~15 mV). Earlier observations of this nature were interpreted as the consequence of a gradual adsorption of the phosphate ion at dissolution sites resulting in physical blocking of the surface (71, 75).

From the stabilization times of the current and rest potential curves, the rate of formation of the protective film in phosphoric acid seems to depend somewhat on the availability of oxygen in the solution (stabilization achieved in ~150 and 200 minutes in un-purged and purged solutions respectively).

None of the tests in phosphoric acid show any significant amount of insoluble corrosion product. In fact, passive films on these samples are so thin that sufficient powder could not be collected for infrared analysis by conventional methods (~0.2 mg). There was however, a clear difference in the physical appearance of the films formed in purged and un-purged solutions. Aerated solutions produced whitish and powdery layers, whereas a transparent, glassy thin film was formed in the purged solutions.

Solutions of phosphoric acid are known to produce passive films on the steel surface composed of the products FePO_4·4H_2O and Fe\((PO_4)\cdot8H_2O\), as well as the acid ferric phosphate FeH\((PO_4)\cdot(105)\). The ferric phosphate was suggested...
ted to form when solutions contained only the ferric ion. It is likely that in the purged tests the only product formed is the Fe(PO$_3$)$_4$·8H$_2$O, due to the absence of ferric ions. The ferric phosphates would form in the aerated solution upon the oxidation of ferrous ion to ferric.

**Inhibition of the corrosion of weathering steel by phosphoric acid surface treatment**

The inhibitor treatment used in atmospheric exposure testing was the surface application of 25% phosphoric acid prior to exposure. This caused considerable reduction in corrosion rates compared to bare steel, as illustrated by field testing results in figure 1.4.1.

In potentiodynamic testing, phosphoric acid surface treatments produced corrosion currents that were about equal to those produced in the potentiodynamic testing of bare steel, Table 1.3.6 and figures 1.3.21 and 22. Anodic Tafel slopes of approximately 75 mV in Table 1.3.6 leads one to suggest a dissolution mechanism similar to that determined by Kuo and Nobe(62) for the dissolution of iron in acidic chloride solution. The following reaction sequence and rate determining step account for the observed Tafel slope:

\[
\begin{align*}
\text{Fe} + \text{H}_2\text{O} & = \text{Fe} \cdot \text{H}_2\text{O}(\text{ads}) \\
\text{Fe} \cdot \text{H}_2\text{O}(\text{ads}) + \text{Cl}^- & = \text{FeClOH} (\text{ads}) + \text{H}^+ + e^- \\
\text{FeClOH} (\text{ads}) & \rightarrow \text{FeClOH} + e^- \quad \text{RDS} \\
\text{FeClOH} + \text{H}^+ & = \text{Fe} + \text{Cl}^- + \text{H}_2\text{O}
\end{align*}
\]
where the formation of chloro complexes are again invoked due to the direct participation of Cl ions in the elementary ionization process.

Weathering steel does not passivate by phosphoric acid surface treatments, as shown by the E vs. i tests (1.3.22 and 23.). Potentiostatic tests demonstrate also that currents and the negative shift in the rest potential obtained for surface treatments are significantly lower than those for bare weathering steel (figures 1.3.15 and 1.3.16.). This confirms the results from field exposure testing. The four parameters i, E(rp), pH and [Fe(II)]/[Fe(III)] show the same characteristic variation with time, as found in bare weathering steel. All parameters begin to stabilize at approximately 400 minutes for unpurged and 200 minutes for purged solutions. The negative shift in the rest potential is ~100 mV and ~50 mV for the unpurged and purged solutions, respectively. One can conclude that although the basic dissolution steps must be the same, (i.e. the specific adsorption of chloride, complex formation and subsequent hydrolysis of these complexes), inhibition of the corrosion process takes place due to the presence of phosphoric acid. The corrosion products identified at the surface of the steel specimens at the end of the potentiostatic tests were identical to those produced in the potentiostatic tests of bare steel. These were lepidocrocite in the presence of air and the amorphous oxide-hydro-
oxide in the absence of air (figure 1.3.14.).

Among the two main types of inhibition, the postulate of interface inhibition presumes strong physical interaction between the corroding substrate and the inhibitor (96, 97). The inhibitor can either physically block-off the surface by the formation of protective film, or plug-up the active sites. Experience with atmospheric testing of phosphoric acid surface treated weathering steel confirms that a protective, integral iron phosphate film does not form on the steel surface. All evidence points in the direction of phosphate ions in the solution adsorbing to the active dissolution sites on the already present rust films (ferric oxide-hydroxide in the presence of air, amorphous layer in purged solutions) rust films. Figure 1.4.5 shows the infrared pattern for a phosphoric acid treated field sample. The IR pattern is predominantly that of amorphous rust with some of the lepidocrocite peaks also visible. The strongest lepidocrocite peak at 1025 cm\(^{-1}\) however is rather uncharacteristically broad (compare figures 1.3.3 and 1.3.14). The P-O stretching vibrations are also in this region with one peak at precisely 1025 cm\(^{-1}\) (98). The broad band at this wave number could be due to a small amount of phosphate that would be necessary to plug-up an active site on the oxide-hydroxide film inhibiting further dissolution.

The inhibitor efficiency can be calculated using the empirical equation,
\[ e = \frac{[i-i(\text{inh})]}{i} \]  

(14)

where, \( e \) = efficiency

\( i \) = current in the absence of the inhibitor

\( i(\text{inh}) \) = current in the presence of inhibitor

using the values of the current in the potentiostatic test after it has stabilized, one obtains inhibitor efficiencies of 92\% and 99\% for un-purged and purged solutions respectively (figures 1.3.12-13 and 1.3.14-15).

For potentials negative and positive with respect to the potential of zero charge, Habib and Bockris (99) suggest the configuration shown in figure 1.4.6 for the phosphoric acid molecules adsorbed on the surface of an oxide layer. Sato and co-workers also attempted to use their membrane potential model to explain the inhibiting action by phosphate particles in aqueous solution (69). Studies on the ion selectivity of hydrated ferric oxide films with adsorbed \( \text{MoO}_4^- \) showed reductions in the corrosion rate of approximately an order of magnitude. The same was observed for \( \text{WO}_4^- \) adsorbed on \( \text{Ni(II)} \) oxide layers. The authors suggested a similar mechanism for inhibition in the case of \( \text{PO}_3^- \) adsorption on the surface of the oxide. A bipolar precipitate membrane system is created upon adsorption that is shown in figure 1.14. This membrane is bipolarized with an anion selective layer on the metal side and a cation selective layer on the solution side. The diffusion of chloride ions from the solution side would
thus be impeded resulting in the observed rectifications in the corrosion current. The results of Ruetchi and Pavlov(100,101) confirmed the inhibition of lead by adsorption of solution anions on surface precipitate films.

If one assumes an indifferent type of adsorption invoked by Sato et al., where the process is not irreversible, the surface coverage and concentration of the inhibitor can be used to make estimates of the free energy of adsorption. The Langmuir isotherm relates the surface coverage, concentration of inhibitor species and free energy in the following expression;

\[ \frac{c}{55.5} \exp \left[-\frac{G(\text{inh})}{RT}\right] = \frac{\Theta}{1-\Theta} \]  

(15)

where \( c \) is the concentration of inhibitor, and \( \Theta \) is the surface coverage.

In the case of indifferent adsorption the inhibitor efficiency can be taken equal to the surface coverage, (102). Using the values calculated above for the efficiency of inhibition and concentration of 25% (=0.26M), the Gibbs free energy of adsorption is calculated to be -4.6 kcal/mol. Several modifications are in order however, such as a lower value for the concentration of the inhibitor. The concentration of inhibitor is much lower than 25% due to the surface application of the phosphoric acid and not solution. Approximately 2 ml of the inhibitor was applied on the surface which after drying was then immersed into a
test solution of 500 ml. The inhibitor concentration could then be taken to be 0.001 M. The free energy of adsorption calculated with these values would yield -7.8 kcal/mol. It is quite unlikely however that the surface coverage by the phosphate ion is as high as 92%. If one uses the value for the surface coverage obtained by Habib and Bockris for 0.001 M phosphoric acid solution (~42%, using the Temkin adsorption isotherm), the free energy of adsorption is calculated to be -6.3 kcal/mol. Listed below are the free energies of adsorption of several solution species calculated by Andersen and Bockris (103):

<table>
<thead>
<tr>
<th>ion</th>
<th>free energy of adsorption (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>+ 13.7</td>
</tr>
<tr>
<td>+</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>+ 2.7</td>
</tr>
<tr>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>- 7.3</td>
</tr>
<tr>
<td>-</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>+ 8.9</td>
</tr>
<tr>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>- 9.0</td>
</tr>
<tr>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>- 11.4</td>
</tr>
<tr>
<td>-</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>- 13.1</td>
</tr>
</tbody>
</table>

Keeping in mind the assumptions made in calculating the free energy value for the phosphate, in a situation where the solution chloride and phosphate species were competing for adsorption at the steel surface, the chloride would have had a significant advantage given the value of
its free energy of adsorption. By pre-treating the surface, however, the phosphate ions are made to adsorb first before the surface is exposed to the chloride solution. This would probably explain the observation that in the field exposed samples, the phosphoric acid induced films degrade slowly in time to other forms of more crystalline rust phases. At what time this degradation commences would depend on the concentration of the chloride environment encountered.
Fig. 1.4.1. Weight loss curves for sheltered location coupons at Leesville bridge.
<table>
<thead>
<tr>
<th>NaCl conc.</th>
<th>m</th>
<th>LOG m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 %</td>
<td>6.2</td>
<td>0.79</td>
</tr>
<tr>
<td>0.1 %</td>
<td>11.7</td>
<td>1.1</td>
</tr>
<tr>
<td>1 %</td>
<td>73.9</td>
<td>1.86</td>
</tr>
<tr>
<td>5 %</td>
<td>500</td>
<td>2.69</td>
</tr>
<tr>
<td>10 %</td>
<td>490</td>
<td>2.69</td>
</tr>
<tr>
<td>15 %</td>
<td>512</td>
<td>2.70</td>
</tr>
</tbody>
</table>

Table 1.4.1. The effect of chloride concentration on m.

<table>
<thead>
<tr>
<th>TYPE OF TEST</th>
<th>(average metal loss) MPY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical</td>
<td>1% NaCl 99.7</td>
</tr>
<tr>
<td></td>
<td>0.1% NaCl 72.8</td>
</tr>
<tr>
<td>Salt Fog</td>
<td>41.0</td>
</tr>
<tr>
<td>Immersion</td>
<td>2.5</td>
</tr>
<tr>
<td>Atmospheric Exposure</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Table 1.4.2. Comparison of metal loss in accelerated v.s. atmospheric tests.
Fig. 1.4.2. The effect of displacement from $E(oc)$ on $'m'$.
Fig. 1.4.3. Chloride concentration v.s. m.
**Fig. 1.4.4.** IR pattern of atmospheric exposure coupon surface treated with 25% phosphoric acid.

**Fig. 1.4.5.**

Schematic model of adsorbed phosphoric acid molecules separated by adsorbed water molecules.
PART TWO

TRANSFORMATION STUDIES

ATMOSPHERIC EXPOSURE AND LABORATORY TESTING

2.1. INTRODUCTION

The most conspicuous form of the degradation of materials, atmospheric corrosion, manifests itself in a variety of phases both amorphous and crystalline. Many different oxides and hydroxides of iron have been identified, primarily with the techniques of X-ray diffraction, Mössbauer spectroscopy, Raman spectroscopy and infrared spectroscopy. The oxyhydroxides of iron, FeOOH, magnetite, Fe₃O₄, hematite Fe₂O₃, maghemite Fe₂O₃, and some of the less ordered phases such as green rusts as precursors to these crystalline phases and a form of amorphous corrosion product have all been detected on mild and low alloy steels after exposure to atmosphere [107-114]. It has been suggested that there are two layers of rust formed during atmospheric corrosion. Of these, the outer layer grows during the wet cycle (i.e. rain and moisture), and an inner layer during the dry periods. The rusting is generally thought to start by the formation of nodules and blisters that eventually rupture. The insides of these blisters usually reveal the intermediate forms of rust known as the green rusts or green complexes.

Once these green complexes are formed, further corrosion is controlled by their existence. For this reason
Misawa and coworkers closely studied the formation of these intermediate forms which they called green rust 1, green rust 2, green complex 1 and green complex 2 (107-109). They suggested the following reaction scheme for the formation of these phases:

\[
\begin{align*}
\text{Fe(OH)}_2 & \xrightarrow{\text{a}} \text{green rusts I and II} \\
\text{FeOH}^+ & \xrightarrow{\text{a}} \text{green complexes (G.C.I and II)} \\
\end{align*}
\]

where \(a\) stands for aerial oxidation.

These authors found that upon the aerial oxidation of neutral and slightly alkaline ferrous sulphate solutions, the aqueous \(\text{Fe(II)}-\text{Fe(III)}\) complex, named green complex 2 was formed. This would be followed by the oxidation of \(\text{FeOH}^+\) and the formation of green rust 2. The \(\text{Fe(II)}/\text{Fe(III)}\) ratios in GC2 and GR2 were found to be the same, i.e. 1. On the other hand both GC1 and GR1 that form in slightly alkaline solutions containing chloride ions, were found to have \(\text{Fe(II)}/\text{Fe(III)}\) ratios of 2. The fact that the GRs could be prepared by the precipitation of GCs suggested that their configurations were similar. The GCs are represented by,

\[
\begin{align*}
[\text{Fe(II)Fe(III)}_2 \text{(OH)}_{2x-y}]^{(7-2x-y)+} \\
[\text{Fe(II)Fe(III)}_x \text{(OH)}_y]^{(5-2x-y)+}
\end{align*}
\]

for GC1 and GC2 respectively.

Further oxidation of the green intermediates pro-
duced the many oxide and oxide-hydroxide forms that are found as atmospheric corrosion products on structural steel.

Lepidocrocite was explained to form by the same authors in the shape of acicular crystals by the following reaction,

\[
\begin{align*}
\text{Fe(OH)}_3 & \xrightarrow{\text{a}} \text{green rusts I and II} \\
&(\text{h}) \\
&\downarrow \quad \downarrow
\\
\alpha & \quad \gamma - \text{FeOOH.} \\
&(\text{h+c}) \\
&\downarrow \quad \downarrow
\\
&\text{the subscripts s and r denoting slow and rapid oxidation.}
\end{align*}
\]

The presence of ash and gypsum is thought to favor the formation goethite(\(\alpha - \text{FeOOH}\)), whereas chloride favors the formation of akagaenite(\(\beta - \text{FeOOH}\)).

\(\delta - \text{FeOOH}\) is considered to form as a result of the topotactic transformation between two solid phases of hexagonal cubic structure following the reaction,

\[
\begin{align*}
\text{Fe(OH)}_3 + 1/4 \text{O}_2 & \xrightarrow{\text{V}} \delta - \text{FeOOH} + 1/2 \text{H}_2\text{O.} \\
&(\text{h}) \\
&\downarrow \quad \downarrow
\\
&\text{\(\delta - \text{FeOOH}\) could also be formed by the violent oxidation of the GCs and GRs;}
\end{align*}
\]

Misawa et al. suggested the reaction shown earlier in the case of lepidocrocite, for the formation of magne-
The changes in oxidation state and packing sequence of oxygen layers associated with the transformations of green intermediates are shown on Table 2.1.1.

Although thermodynamic considerations suggest that Fe(OH)$_2$ transforms spontaneously to magnetite and lepidocrocite, structurally this transformation seems highly unlikely considering the hydroxide has hcp packing and both magnetite and lepidocrocite have cubic packing for the oxygen layers. The alternative would be the stepwise increase of cubic layers of oxygen by the presence of intermediate phases. The green intermediates with their mixed hexagonal and cubic layers of oxygen, would thus play this role.

Bernal et al. (115,116) determined the crystal structures and lattice constants for most of the rust phases and these are given in Table 2.1.2.

After studying weathering steel surfaces exposed to the atmosphere for 2.5 years as well as synthetically produced samples under aqueous conditions, Misawa proposed the following sequence for the overall rusting process:

\[
\begin{align*}
\text{dissolution} & \quad \text{2+ hydrolysis} & \quad \text{+ oxidation and} \\
\text{Fe} & \quad \text{Fe} & \quad \text{FeOH} & \quad \text{precipitation} \\
\text{dissolution and} & \quad \text{solid state} & \quad \text{amorphous ferric} & \quad \text{oxyhydroxide} \\
\gamma\text{-FeOOH} & \quad \text{precipitation} & \quad \text{oxyhydroxide} & \quad \text{transformation} \\
\text{FeO (OH)} & \quad x & \quad 3-2x \\
\end{align*}
\]

Keiser and coworkers [117,118] used Raman spectroscopy to identify the oxyhydroxides $\alpha$ and $\gamma$-FeOOH and the
main atmospheric corrosion products whereas Leidheiser et al [113] determined $\alpha$-FeOOH to be the initial product transforming in time to $\alpha$-FeOOH and $\gamma$-Fe$_2$O$_3$. Swedish workers [145] using Mössbauer spectroscopy found $\alpha$-FeOOH and $\gamma$-FeOOH to be the main constituents in the rust formed on bold-exposed steel panels, but found significant amounts of $\beta$-FeOOH in marine atmospheres.

To gain a better understanding of the thermodynamic laws governing the stability of various rust forms, Misawa constructed the potential-pH (Pourbaix) diagrams [107]. These theoretical considerations helped to determine the necessary pH conditions for the formation of various phases, but results from atmospheric tests failed to follow the predictions of the Pourbaix diagrams. The formation and transformations of phases in the Fe-H$_2$O system depended not only on thermodynamic relationships of pH and potential, which could be quite complex under atmospheric exposure conditions, but to a great extent on the oxidation rate of $2^+$ Fe and the structure and composition of initial and intermediate rust forms.

Common oxides and oxyhydroxides of iron are of interest to mineralogist, and soil scientists because of their role in soil physico-chemical processes. This can be seen in the volume of contributions they have made in the literature on the formations and transformations of akagaenite and lepidocrocite [120-126], crystallochemical studies [115-116,127-
Topochemistry, the emphasis in the majority of minerological and geological work, involves the reactions and structural relationships of the solid phases, and not transformations of these phases under aqueous conditions. $\alpha$ and $\beta$ oxide-hydroxides are two of the most important forms and have been investigated extensively.

**FORMATION AND TRANSFORMATIONS OF LEPIDOCROCITE**

Misawa and coworkers (107) showed that $\alpha$-FeOOH was one of the main products of atmospheric corrosion of steels in neutral to slightly acidic solutions. Rapid aerial oxidation of 'green complexes' containing both Fe and $3^+$ Fe produced the lepidocrocite with a disordered cubic arrangement for oxygen shown in figure 2.1.1. The green complexes could be skipped over in slightly acidic solutions by the following reaction scheme, again producing $\alpha$-FeOOH.

\[
\text{FeOH} \xrightarrow{\text{aerial oxidation}} \text{Fe(OH)} \quad \xrightarrow{\text{2 HO}} \quad \text{FeO-Fe-OH}
\]

This lepidocrocite upon heating at 150°C in alkaline solution, transformed to goethite ($\alpha$-FeOOH). Due to structural incompatibilities this reaction is feasible only through dissolution and re-precipitation of an amorphous phase fol-
owed by nucleation and growth of $\kappa$-FeOOH [107]. Misawa used X-ray diffraction as the main analytical technique and infrared spectroscopy as complementary.

Bernal and coworkers [115, 116] called several solid-state transformations of iron oxides and hydroxides topotactic indicating that they took place not by nucleation and growth processes, common to phase transformations, but by rearrangement and re-stacking of atoms, resulting in definite structural relationships between the parent and product phases [129]. These authors found that $\kappa$-FeOOH started losing its water upon heating at around 180 °C and was completely converted to the oxide form $\gamma$-FeO at around 290 °C. The topotactic solid-state transformation of $\kappa$-FeOOH to $\gamma$-FeO, i.e., from the orthorhombic to cubic spinel structure, was proposed to proceed solely by removal of half of the hydroxyl groups, resulting in contraction in the [010] direction and a shift of oxygen along [100] (figure 2.1.2). Upon further heating to above ~300 °C, lines belonging to $\alpha$-FeO, haematite, began to appear. Bernal et al. concluded from diffraction data the formation of haematite was subsequent to that of maghemite due to the orientation relationship between the two demonstrated schematically on figure 2.1.3.

Cresser and Livesey [130] found the following reactions and temperatures for the $\kappa$-FeOOH transformations:
Curiously, these authors have reported no significant information from the near infrared spectrum of these phases. De Villiers and Van Rooyen [123] confirmed the same sequence except for a lower temperature of 460 °C for the maghemite to haematite transformation. Some controversy exists over the significance of water in these transformations. Ozdemir and Banerjee [131] claimed water plays no important role in the stabilization of maghemite, whereas David and Welch [132] concluded that due to the defect structure in the spinel, water was essential to the stability of these structures. Kordes [133] found similar result for γ-alumina that has a structure closely related to γ-ferric oxide. Most of these workers used X-ray diffraction as the main analytical technique and IR and Raman spectroscopies as additional tools.

A number of investigators have used the Mossbauer technique for the identification of transformations in rust phases [137-139], but the usefulness of this technique was more apparent when used in conjunction with infrared spectroscopy [134]. Since atmospheric corrosion is essentially an aqueous process, the need to understand the role of water in the various transitions seems clear. Infrared spectroscopy with the wealth of information it provides on all states
of water in the structure, adsorbed, bounded and lattice, is invaluable in this respect.

**FORMATION AND TRANSFORMATIONS OF \( \beta \)-FeOOH (AKAGAENITE)**

\( \beta \)-FeOOH, lying rather outside the general scheme of transformations of iron oxides and hydroxides, is also very rarely found in the mineral form [121,126]. It is formed by the slow hydrolysis of Fe\(^{3+}\) ions in solutions containing chloride. Perhaps due to its rarity, it is one of the least studied of the family of iron oxides also. The crystal structure was determined to be that of hollandite (\( \kappa -\)MnO\(^2\)) [135,136], with extremely uniform pores running through the structure. The \( \kappa -\)MnO\(^2\) or hollandite structure is shown in figure 2.1.4 as a projection on the (001) plane of the compound. Fe\(^{3+}\) ions are surrounded octahedrally by six O\(^2-\), OH ions. The octahedra are then linked to form double bonds parallel to the c-axis. The rows of fused octahedra contain Cl ions. The pore structure was suggested by Music et al, to be stabilized by the presence of large ions such as Cl or F\(^-\) [136]. The uniform pore structure and the dimensions of the pore were later confirmed by Mossbauer work [137-139]. Figure 2.1.5 shows a drawing of the cigar shaped akagaenite. Heating of this compound transformed it to haematite which could only occur by a dissolution and renucleation process. However, Mackay [140] suggested that the DTA record of the transformation gave endothermic peaks at around 250\(^{\circ}\)C indicating some
reaction that was unaccounted for. Heating the material in the beam of an electron microscope revealed the formation of a spinel phase, judging from the diffraction pattern. Mackay speculated that this spinel phase was $\gamma$-Fe$^{2+}$O or FeO$_{2+3}$ which when topotactically transformed to $\alpha$-FeO$_{2+3}$ produced the endothermic peak. Furthermore, Mackay suggested that the hollandite structure of $\beta$-FeOOH could be easily transformed to a spinel by the migration of the Fe ions to the tetrahedral sites and some adjustments in bond distances. If this is so, then it would make the $\beta$-FeOOH to $\alpha$-FeO$_{2+3}$ transformation a series of topotactic solid state reactions.

Gallagher [141] found that heating $\beta$-FeOOH in vacuum at about 170°C produced a phase with a similar X-ray diffraction pattern, but slightly different IR absorption pattern indicating the formation of the oxide from the oxide-hydroxide by the removal of water molecules in the pores. He called this phase $\beta$-FeO$_{2+3}$ and showed that it transformed to a spinel phase on further heating at 200°C, which Gallagher assumed was FeO$_{3+4}$ from the X-ray diffraction data. In air, however, $\beta$-FeOOH did not transform to $\beta$-FeO$_{2+3}$ completely until heated to 400°C.

All these observations seem to indicate that whenever possible, the solid state transformations of the rust phases will proceed by the minimum restructuring of the original crystals. Another important point that can be shown from a consideration of the literature is the importance of
water within the structure in various forms and its role in stabilizing or de-stabilizing, making possible certain transitions. Infrared spectroscopy will be shown to be an invaluable tool in throwing light on the gradual time-dependent transformations of these phases and provide crucial information on the significance of water.
Table 2.1.1. Packing sequence of oxygen

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mineral Name</th>
<th>Space Group</th>
<th>Dimensions (Å)</th>
<th>Z</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe₂O₃</td>
<td>Hematite</td>
<td>R3c</td>
<td>a = 5.0345, c = 13.749</td>
<td>6 (hex.)</td>
<td>H.c.p. oxygen with Fe⁺⁺ in octahedral positions.</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Magnetite</td>
<td>Fm3m</td>
<td>a = 8.3963 (18 C)</td>
<td>8</td>
<td>F or Cl necessary for formation.</td>
</tr>
<tr>
<td>γ-Fe₂O₃</td>
<td>Goethite</td>
<td>Pbnm</td>
<td>a = 8.338</td>
<td>10</td>
<td>NaCl type.</td>
</tr>
<tr>
<td>FeO</td>
<td>Wüstite</td>
<td>Cmcm</td>
<td>a = 4.387, c = 12.51</td>
<td>4</td>
<td>Tetragonal.</td>
</tr>
<tr>
<td>α-FeOOH</td>
<td>Goethite</td>
<td>Pbnm</td>
<td>a = 4.387, c = 12.51</td>
<td>4</td>
<td>Tetragonal.</td>
</tr>
<tr>
<td>β-FeOOH</td>
<td>Lepidocrocite</td>
<td>Cmcm</td>
<td>a = 3.301, c = 24.4</td>
<td>4</td>
<td>Tetragonal.</td>
</tr>
<tr>
<td>γ-FeOOH</td>
<td>Lepidocrocite</td>
<td>Cmcm</td>
<td>a = 3.301, c = 24.4</td>
<td>4</td>
<td>Tetragonal.</td>
</tr>
<tr>
<td>δ-FeOOH</td>
<td>Lepidocrocite</td>
<td>Cmcm</td>
<td>a = 3.301, c = 24.4</td>
<td>4</td>
<td>Tetragonal.</td>
</tr>
<tr>
<td>Fe(OH)₂</td>
<td>Chalybite</td>
<td>R3c</td>
<td>a = 4.711, c = 15.436</td>
<td>2</td>
<td>Calcite structure.</td>
</tr>
<tr>
<td>Fe(OH)₃</td>
<td>Chalybite</td>
<td>R3c</td>
<td>a = 4.711, c = 15.436</td>
<td>2</td>
<td>Calcite structure.</td>
</tr>
</tbody>
</table>

Table 2.1.2. Crystal structures of the oxides and hydroxides of iron.
Projection of the lepidocrocite crystal. \( \chi \)-FeOOH is orthorhombic but is based on a fcc framework of oxygen. The plane of the figure is (100) of fcc.

A comparison of \( \chi \)-FeOOH and spinel structure.
Fig. 2.1.3.
Orientation relationship in the transformation of lepidocrocite (L) to maghemite (M) to haematite (H).

Fig. 2.1.4. Projection of the hollandite structure.
Fig. 2.1.5. A drawing of the cigar shaped somatoids of akagaenite. One of the crystals is blown-up to show a unit cell.
2.2 EXPERIMENTAL

Field Exposure Testing

The experimental work for this study was mostly field related, consisting of two parts—treatment and sample collection from on site locations on the bridges and treatment and sample collection from steel coupons arranged in racks and left at the bridge sites at chosen locations. The latter were later brought to the laboratory periodically for rust collection and retreatment. The surfaces were prepared in seven different ways for atmospheric exposure, on selected site locations on the bridges as well as on field coupons. These were:

Trt. 1. Sand blasted steel surface

Trt. 2. Sand blasting (SB) + treatment with 25 % phosphoric acid (PA).

Trt. 3. SB + treatment with a mixture of 25 % PA and benzoic acid (BA) (12.5 % each).

Trt. 4. Wire brushing (WB) + first treatment with 10 % tannic acid (TA) + second treatment with 25 % PA.

Trt. 5. WB + first treatment with 10 % TA + second treatment with a mixture of 12.5 % PA and 12.5 % BA.

Trt. 6. WB + treatment with 10 % TA.

Trt. 7. Wire brushed surface.

(Wire brushing applied on the bridge was replaced by acid pickling for field coupons)

Both coupons and surfaces on bridge sites were
treated by first spraying and then spreading the acids by paint brushes to assure uniformity. In the case of two successive treatments, for instance the first treatment with tannic acid and the next with phosphoric acid, the second one was not applied before the first treatment had completely dried.

The coupons in the rack were 3"x5" each whereas location treatments were performed on areas approximately 1 foot by 1 foot or 2 feet by 2 feet.

Powder samples were scraped off from the surfaces and stored in sealed, well marked envelopes and taken for pelletizing using the KBr technique for infrared spectroscopy. The infrared spectrophotometer was the Perkin-Elmer Model 283 used in all the previous work in this laboratory \[146,151,152\], that produced all the data on standard amorphous and crystalline rust forms and their transformations. Careful analysis of the patterns, that are extremely detailed fingerprints of the absorption spectra, was done with the experience accumulated throughout the project dealing with a great number of samples. Standard IR spectra of all rust phases are illustrated on figure 2.2.1.

**Laboratory Testing**

Methods for the preparation of synthetic lepidocrocite and akagaenite are numerous and can be found described in the literature \[134,142-144\]. Not all of the preparation methods gave good results, however, and the ones
chosen for this study were of Fricke and Zerweck given in [123] for lepidocrocite and Mackay [140] for akagaenite.

\( \gamma \) -FeOOH was best prepared by dissolving 7.0 gm of FeSO\(_4\) \( \cdot \) 7H\(_2\)O and 1.5 g of NH\(_4\)Cl in 1 lt. of water and then mixing it with a solution of 11.25 g of Na\(_2\)S\(_2\)O\(_4\) \( \cdot \) 5H\(_2\)O in 2 lts. To this was added 2.75 g of KIO\(_3\) in 500 ml. The whole procedure was carried out at room temperature.

\( \beta \) -FeOOH was prepared by the slow hydrolysis of 0.05 M FeCl\(_3\) solution at 75 \( ^\circ \) C in about 12 hrs.

The synthesized oxyhydroxides were initially confirmed by X-ray diffraction (Mo-K\( \alpha \)) and infrared spectroscopy and observed under the scanning electron microscope (SEM).

Transformations were tried at progressively higher constant temperatures to find the optimum temperature at which the reactions were not too fast to prevent intermediates from being observed but not too slow either such that detectable changes could be observed in a given meaningful time. The detailed "fingerprinting" by the infrared technique was most useful in following the transformations and dehydration of the oxyhydroxides. The in-vacuum transformations were followed utilizing a vacuum furnace. The temperatures used were measured accurate to \( \mp 3 \) deg. C. The instrument was calibrated with a standard polystyrene film from 4000 cm\(^{-1}\) to 200 cm\(^{-1}\).
Fig. 2.2.1. Standard IR patterns of rust phases found in the atmosphere.
Fig. 2.2.1. Standard IR patterns continued.
2.3. RESULTS AND DISCUSSION

Field Exposure Testing

Since this study aims to investigate the mechanisms of atmospheric rusting and to follow the transformations, it is best to present and discuss the results in a time dependent fashion. It is also useful to present and discuss the results for bridge site location treatments and coupons separately due to additional parameters that may come into play, such as the fact that coupons are necessarily small in size and are held in racks to facilitate their return back to the laboratory, whereas the treatments on the bridges entailed treating only very small areas on beams and plates. Such portions on large surfaces would encounter different heat transfer and water condensation conditions, than the field coupons in racks.

The earliest analysis of samples in the racks located at various bridge sites was 1 month; therefore time dependent data starts first from the identification of rust after 1 month exposure. The specimens on the racks brought back to the laboratory were retreated, reinstalled in the racks and reexposed at the same bridge sites for various periods of time. All the racks were subsequently brought back at the end of 18 months after exposure to different time periods. Data for reapplication of chemicals after some initial exposure times were also collected. For instance during the visit on the 1st year of the exposure at the
bridge sites, specimens on one of the racks would be re-treated, i.e. acids reapplied right there on the bridge site. In this way the effect of re-treatment was studied when the racks were brought back later, i.e. after 15 and 18 months total exposure. Therefore, the term retreatment is used in reference to such retreatments on previously treated and rusted surfaces, for instance those given after one year exposure. Retreatments were given after 6 months and after one year from the initial dates of applications of chemical on the steels in the bridges. Specimens are identified suitably, such as 2 Y. A.T., 1 Y. R.T. which means 2 years from original application with a subsequent retreatment after 1 year.

Time dependent formation and transformations of atmospheric rust phases on weathering steel coupons for exposure times of 1, 3, 6, 9, 12, 15 and 18 months can be followed for chosen bridges and surface treatments in Table 2.3.1. Selected infrared patterns showing the formation and gradual transitions of the phases up to 18 months of exposure can be seen in Fig 2.3.1-a,b,c.

It can be seen from the results summarized in Table 2.3.1 that the main atmospheric corrosion products on weathering steel coupons consist of the phases, $\gamma$ and $\delta$-FeOOH, $\gamma$-Fe $O_3 H_2O (\chi)$, their amorphous equivalents, the ferrihydrite (F) and the two amorphous forms-AM the amorphous mixture consisting of $\chi$-FeOOH (am) + $\delta$-FeOOH (am) +
F(am) and AB, the amorphous bulk suggested to be similar to the early amorphous aggregate that eventually precipitates the crystalline phase in Misawa's study [108]. The general pattern of the progress of atmospheric rusting seems to start from the formation of the amorphous mixture. The rate at which this transforms to the higher degree of crystallinity but still not crystalline $\gamma$-FeOOH ($\gamma$) and $\delta$-FeOOH ($\delta$) can be seen to be different for different surface treatments. It could be observed for instance that surface treatments with phosphoric acid, and phosphoric acid – benzoic acid mixture have retarded the speed with which transformations proceed to crystalline phases in various samples (Table 2.3.1-a). Sand blasted specimens passed through from amorphous analogs to the crystalline $\gamma^* + \delta$ within a year and these phases persisted to longer time periods. Attention should be drawn to one important form of notation in the Table; the phases listed are in their order of dominance in the IR absorption pattern, i.e. $\gamma^* + \delta$ would be different from $\delta + \gamma^*$ in that in the former $\gamma$ would be the dominant phase and $\delta$ the secondary, whereas in the latter $\delta$ would be the dominant phase and $\gamma$ the secondary. It could be seen that $\gamma^*$ forms first out of the amorphous mixture (AM) and gradually takes second place as the $\delta$ phase becomes more and more dominant in the rust.

There are, however, some phases that appear only at specific bridge locations and some at specific bridge
locations at specific exposure times only. The most obvious of these cases is the formation of ferrihydrite. This phase is found in significant proportions only in samples located at the Leesville and Boeuff river bridges, as can be observed in Tables 2.3.1 and Fig. 2.3.1-c. Leesville bridge is located about 100 miles north of the gulf coast in the coastal regions of the state of Louisiana amidst rural environment. Of all the bridges studied, Leesville (LV) and Boeuff river (BR) bridges are the ones located in what can be called "rural areas". These bridges being far from the coastline, experience negligible chloride contents in the atmosphere. The BR bridge, relatively speaking, is located in a cleaner atmosphere amidst farms and greens, whereas the LV railroad bridge spans over a road and experiences fumes from automobiles. Some bridges, notably Doullout Canal (DC), are located in marine atmospheres with significant amounts of sea salt reaching their surfaces. The other bridges, including Luling (LU) probably receive higher pollutant contents due to being situated near highly industrialized areas of the State of Louisiana, particularly in the vicinity of oil refineries, chemical industries, etc. They also obtain some chloride from the air. These observations are borne out by the earlier chemical analysis of the rust samples [146].

Considered in this context, it can be proposed that the appearance of ferrihydrite in significant propor-
ations in atmospheric rusts only at LV and BR is probably associated with the absence of Cl as well as the general quality of atmosphere. It is common knowledge that rural areas are associated with a more alkaline environment due to farms, nature of the soil etc. [145]. Indeed Ca and Si concentrations are higher on rusts in these bridges relative to the others [146]. It is known that ferrihydrite is stabilized by the presence of Si when it is being precipitated from ferrous solutions [120] and the substantial amounts of ferrihydrite in atmospheric rust can be said to be due to this fact. The ferrihydrite could be found for all treatments and would seem to follow the formation of the amorphous mix (AM) which disappears in time. Treatments 2 and 3, as can be seen in Table 2.3.1 and Fig. 2.3.1, seem to be most favourable to the formation of ferrihydrite, it being the only phase to stabilize after the disappearance of the AM. But in most other treatments on specimens located at the LV bridge $^\ast$ and $\delta$ are also formed out of the AM. These together with the dominant ferrihydrite (F) constitute the final products at the end of 18 months atmospheric exposure, as can be seen for treatment 1 at Leesville in Table 2.3.1. With treatment 6, the transformations were found to be carried one step further by the transformations of F to produce the mixture of $\gamma^\ast + \delta$ as the final phases after 18 months of exposure at this bridge site. In the other bridges, except at Luling, formation of F was suppressed [149].
The hydrated maghemite phase, a fairly common phase encountered in the laboratory salt fog test and also in thick sheet-type of original rust formed on the steels at the Luling bridge [148-149] was not found except for some locations. $\gamma$-Fe O $\cdot$H O was found in dominant amounts in rusts formed on weathering steel at Luling, High Island and Doullout Canal bridges. At Luling it occurred in the two earliest periods of the exposure, namely 6 and 9 months, and vanished from the rust mixture by the first year of exposure. For on-site treatments of the bridge steel itself, this phase is not even detected at the first exposure analysis, presumably because the first samples analyzed had been derived after 6 months exposure. It occurred as a major phase however on the rust from the steel with tannic acid treatments (trt. 6) after 2 years exposure along with amorphous $\delta$ and $\gamma$ in the case of Doullut Canal. Since it was obtained only in certain intermediate times of exposure of steel and was not found in rusts collected after longer time periods it can be inferred to transform to another rust phase. However it is difficult to say with any certainty to which phase it is transforming. It is presumed that it changes to $\delta$-FeOOH. Crystallochemically it should be more feasible for the $\gamma$-Fe O $\cdot$H O with a possible hcp structure of O and OH [149] to transform to the $\delta$-FeOOH form which also has a hexagonal O-OH skeleton [154] rather than the $\gamma$-FeOOH with a cubic oxygen lattice.
This peculiar ghost-like appearance of the phase at the earlier stages of atmospheric corrosion can be explained by the high chloride contents of these sites. As mentioned earlier was found extensively in the laboratory salt fog tests using high chloride containing solutions [148]. Early accumulation of Cl on the surfaces that were not washed off by rain or wind in a dry spell of weather might have created the conditions for the initial transformation of some of the AM or $\gamma$ first formed on the steel to this phase. The phase appears to be highly unstable and transforms in time to $\delta$ (or $\alpha$-FeOOH) forms.

The results from both field coupons and bridge on-site locations agree fairly well. The IR technique is found to be well suited for the analysis of atmospheric rust layer that has several phases, including the amorphous one. The formation of the ferrihydrite in the atmospheric rust is not known [114]. The occurrence of it in significant amounts as a fairly stable phase is a major contribution from this study and IR analysis. The surface treatments, particularly with phosphoric acid, seem to slow down the natural rate of atmospheric corrosion in these steels. They seem to favour the retention of amorphous phases, probably by stabilizing them through inhibiting action, which is the subject of another study [155].
Laboratory Testing

The purities of the synthesized starting materials were confirmed by X-ray and infrared spectra given in the literature [125-125,128-129,140,150], also particularly in the first paper of this series dealing with the many standard forms of rust [151]. For detailed information of the infrared spectra of the rust phases, the reader is referred to the above mentioned papers. Figure 2.3.6 shows the X-ray pattern of pure $\beta$-FeOOH obtained by two different preparations.

Tables 2.3.2(a,b) summarize the temperatures and times of transformations of $\beta$-FeOOH both in air and in vacuum. The various lower and higher temperatures other than the main temperatures at which the transformations were studied can be considered as testing temperatures for determining the optimum temperature of transformation. A critical temperature range was found to exist above which the transformations were too fast for the observations on intermediates to be made or below which the transformations would have taken extremely long times.

The time dependent transformations of $\beta$-FeOOH at several chosen temperatures can be followed in close detail in Fig. 2.3.2(a,b,c) and Fig. 2.3.3.

Time dependent transformations of lepidocrocite can also be seen in the infrared spectra given in Fig. 2.3.4.
Electron microscopy was used to confirm some of the morphologies that were reported in the literature for these phases. Spindle or cigar shaped crystals or somatoids for $\beta$-FeOOH form and other known morphologies, similar to those observed for $\gamma$-FeOOH in atmospheric rusting, can be seen in the micrographs of Fig. 2.3.5.

It can be seen in the tables that, as expected, higher temperatures accelerate the reactions by providing the necessary activation energy, rendering them in fact too fast for analysis of the intermediates in some cases. Thus, for the transformations of $\gamma$-FeOOH in air, the optimum temperature would seem to be 300 C. At 100 C the transformation does not go to completion, i.e. form the most stable phase $\alpha$-Fe $\text{O}_2$ even after very long time of baking, whereas at 400 C the intermediate phase is completely missed even at very short times (Fig. 2.3.4). The $\gamma$-FeOOH gradually transforms to the $\gamma$-Fe $\text{O}_2\cdot\text{H}_2\text{O}$ form and finally to $\alpha$-Fe $\text{O}_2$, which seems to be either totally or incompletely crystalline depending on the temperature of baking. The higher the temperature the better is the crystallinity. The degree of crystallinity can be qualitatively deduced based on the width of the absorption bands [150,151]. For instance one of the prominent absorption bands of $\alpha$-Fe $\text{O}_2$ at around $\nu_1 \approx 550$ cm$^{-1}$ has a half-peak width of approximately 75 cm$^{-1}$ and 50 cm$^{-1}$ at the end of the transformations at 300 C and 400 C respectively, considerably sharper in the latter
(Fig. 2.3.4). This result is taken as a qualitative measure of crystallinity. The transformations of $\chi$-FeOOH in vacuum at 200°C, starts with a broadening of the dominant peaks. A gradual change to an amorphous form of maghamite takes place. This latter phase retains its stability after long hours of baking (fig. 2.3.6). The patterns show also the formation of hydrated maghamite as an intermediate.

Transformations of $\beta$-FeOOH show a similar trend also with respect to the effect of temperature on the reaction rate, both in vacuum and in air. It can be seen from Fig. 2.3.2-C that the final product $\chi$-FeO is only achieved at 230°C and higher temperatures, for example at 500°C, with a similar conclusion reached as in the $\chi$-FeOOH transformation regarding the degree of crystallinity of the $\chi$-FeO, judged by the half-peak width. In air, as in vacuum, the transformation of $\beta$-FeOOH starts by the loss of the H$_2$O allowing it to transform to its oxide form simply by losing its water [141]. This transformation can be followed very accurately by the infrared spectroscopic technique. Fig. 2.3.3 and 2.3.2-b show the progressive disappearance of the absorption peak corresponding to the OH bending frequency of the oxyhydroxide at around $750$ cm$^{-1}$ at baking times of 12, 19 and 25 hours at 170°C in vacuum and 17 hours at 190°C in air, respectively. The X-ray diffraction pattern remains exactly the same, confirming the contention that the transformation $\beta$-FeOOH $\longrightarrow$ $\beta$-
FeO takes place only by the loss of HO from 2 3 channels of the FeOOH structure and without a collapse of the skeleton crystal. FeO then proceeds to transform to the hydrated maghemite \(\alpha\)-FeO H O, which can be observed step by step (Figs. 2.3.2-b and 2.3.3) at the temperatures 170°C and 190°C for both air and vacuum bakes. The transformation in vacuum at 170°C does not proceed much further than the FeO form, whose absorption bands seem to widen out with longer aging times (Fig. 2.3.2-b). This result, which can be interpreted to mean that the material is becoming more amorphous or less crystalline seems to be significant and will be discussed in more detail together with similar phenomena as observed for the transformation of FeOOH in air and of FeOOH in vacuum and air at different baking temperatures.

The characteristic variations in the IR absorption spectra as FeO H O becomes more disordered or less crystalline are also described in Ref [151]. The FeO H O would seem to be quite a stable form of the oxide as it persists for extremely long baking times, 600 hrs. at 190°C (Fig. 2.3.2-b) both in air and in vacuum. This form, previously not well documented, as well as its stability with respect to the other known oxyhydroxides of iron have also been confirmed from the field and laboratory testing of weathering steels in the atmosphere [151-153].

A calculation of the activation energies of seve-
eral of these phase transformations can be attempted, however only to a first approximation due to the estimation of the time periods for completion of the transformations. By using the standard diffusion-based equation for activation energy as a function of times at two different temperatures, one can write:

\[
Q = 1.987 \times \frac{T_1 \times T_2}{T_1 - T_2} \times 2.303 \log \frac{t}{T_2 - T_1}
\]

where temperatures \( T_1 \) and \( T_2 \) are in deg. Kelvin and the activation energy \( Q \) is in cal/mol. Rough estimates of \( Q \) using this equation and the times and temperatures used are given below:

<table>
<thead>
<tr>
<th>Transformation</th>
<th>( Q ) kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma )-FeOOH ( \rightarrow \gamma )-Fe O ( \cdot ) H O ( 2 \ 3 \ 2 ) ( t = 150 ) hr at ( 373 ) K ( ^\circ )</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>( t = 2.0 ) hr at ( 573 ) K 2</td>
</tr>
<tr>
<td>( \chi )-Fe O ( \cdot ) H O ( \rightarrow \chi )-Fe O ( 2 \ 3 \ 2 ) ( 2 \ 3 ) ( t = 30 ) hr at ( 573 ) K ( ^\circ )</td>
<td>6.46</td>
</tr>
<tr>
<td></td>
<td>( t = 2.0 ) hr at ( 673 ) K 2</td>
</tr>
<tr>
<td>( \beta )-FeOOH ( \rightarrow \beta )-Fe O ( 2 \ 3 ) ( t = 10 ) hr at ( 463 ) K ( ^\circ )</td>
<td>3.49</td>
</tr>
</tbody>
</table>
Values around 8 kcal/mole are quoted in the literature \[117\] for the transformation $\gamma$-Fe$_2$O$_3 \rightarrow \alpha$-Fe$_2$O$_3$. The calculated value is fairly close for the hydrated form of the oxide. However, one would expect for the topotactic transformation $\beta$-FeOOH to $\beta$-Fe$_2$O$_3$ that only involves the escape of water from the pores, a value lower than 3.49 kcal/mol, but still the value seems to be of the right magnitude.

Based on the results obtained in this study, which are enumerated in the Table 2.3.2 and shown in the Figures 2.3.2-3 the following sequences of transformations can be deduced:

In air and in vacuum
\[
\gamma \rightarrow \gamma(\text{am}) + \gamma$-Fe$_2$O$_3 \rightarrow \gamma(\text{am}) (v)
\]

$\gamma \rightarrow \gamma(\text{am}) \rightarrow \gamma \rightarrow \gamma(\text{am}) \rightarrow \alpha(\text{am}) \rightarrow \alpha (\alpha)$

In air and in vacuum

$\beta \rightarrow \beta$-Fe$_2$O$_3 \rightarrow \beta$-Fe$_2$O$_3(\text{am}) \rightarrow \gamma(\text{am}) \rightarrow \gamma \rightarrow \gamma(\text{am}) \rightarrow \alpha(\text{am}) \rightarrow \alpha$

$[\gamma = \gamma$-FeOOH, $\gamma = \gamma$-Fe$_2$O$_3$, H O, $\alpha = \alpha$-Fe$_2$O$_3$, $\beta = \beta$-FeOOH, (am) = not well crystallized ]$

Occurrence of the not well crystallized states for all the intermediate phases can also be recognized.

As can be noted and also mentioned earlier, some of the transformation results seem to indicate trends, espe-
cially with respect to the changes in the degree of crystallinity, that are contradictory to conventional understanding. One would expect the degree of crystallinity to increase as the aging times are increased. This seems indeed to be the case whenever a stable final product appears in the transformation sequence, such as $\alpha$-Fe $\text{O}$, seen in Fig. 2.3.4 for bakes at $300^\circ\text{C}$ and $400^\circ\text{C}$ or vacuum heating of $\beta$-FeOOH at $190^\circ\text{C}$ which yields $\chi$-Fe $\text{O}$.H $\text{O}$ with increasing crystallinity after very long aging times (Fig. 2.3.3). This tendency is reversed however as we examine not the final product but the intermediates. In the transformations of both $\beta$-FeOOH and $\chi$-FeOOH, the intermediates exhibit higher degrees of crystallinity as they form at first from the amorphous or disordered state and move towards more amorphous (wider peaks) structures as they near the next step in the transformation. This can be seen for both $\beta$-Fe $\text{O}$ baked at $170^\circ\text{C}$ (Fig. 2.3.3) and $\chi$-Fe $\text{O}$.H $\text{O}$ baked at $190^\circ\text{C}$ (Fig. 2.3.2-b) and $200^\circ\text{C}$ (Fig. 2.3.2-c), which are the intermediate phases in the transition.

It is widely accepted that most of the phase transformations in the oxides and oxyhydroxides of iron are of topotactic nature, as discussed in the introduction to this paper. Even the $\beta$-FeOOH to $\alpha$-Fe $\text{O}$ transformation which was thought to be lying outside this general process for transformations, was shown by Gallagher and Mackay [126,141] to involve perhaps more than one intermediate
steps, also confirmed by this study, and may also consist of the rearranging and shifting of atoms and atomic planes, i.e. it is topotactic in nature. Thus if we think of the transformation as one long chain of steps from one stable form to another, it may not seem that unconventional to think of the intermediates as necessarily moving from a less disordered to a more disordered state of existence, especially in the oxygen and OH-ion lattice, preparing for the onset of the next crystallographic form.

This study, however, shows conclusively that the reaction from lepidocrocite to haematite does not necessarily pass through the formation of maghemite as was described by others [115,125,129]. The finding of the hydrated form of this oxide as the intermediate is a new result, and the nature and mutual structural relationship of the parent, the intermediates and final phases need to be reexamined much more thoroughly. More structural information is needed on the nature of bonding, the role of H O, etc., in the corrosion product designated as $\gamma$-Fe O $\cdot$ H O that seems to appear $2$ $2 2$ in the intermediate stages during corrosion of weathering steels in sheltered locations.

In general though, except for the fact that transformations occurred at temperatures lower than those reported in the literature, the formation of the intermediate $\beta$-Fe O and the final product haematite were confirmed. Infrared spectroscopy has proved to be extremely useful in
following transformations, once the variety of rust phases have been identified clearly [151]. Infrared spectroscopy is probably the only technique that gives unambiguous information on the important role of water, in its various forms—adsorbed, bound and lattice— in the structures of the rust phases, which is so important for understanding the atmospheric rusting mechanisms.
**TABLE 2.3.1**

**ANALYSIS OF IR PATTERNS OF RUSTS SHOWN IN FIG. 2.3.1**

<p>| Trt. Steel Grade Rusting History Phase present (dominant phase given first) ref. |
|-------------------------------------------------|------------------------------------------------|
| No.                                            | Figure |
| 7 Kw A 2 YAT am.χ + AM + tr.χ* *     | 1-a     |
| 7 US A 1 YAT χ + χ * | (b) |
| 7 Kw A 1 YAT am.χ + AM + tr.χ* *     | (c) |
| 7 Kw A 2 YAT am.χ + tr.χ * | (d) |
| b) At Doullut Canal Bridge on location. |
| 7 US A 1 YAT AM + χ + tr.χ *     | (e) |
| 7 US A 2 YAT AM + χ + tr.χ *     | (f) |
| 6 A 6 MAT AM + am.χ + tr.χ * * | 1-b (a) |
| 6 A 1 YAT AM + am.χ + tr.χ * *     | (b) |
| 6 A 1 YAT AM + am.χ + tr.χ * *     | (c) |
| 6 A 2 YAT am.χ + χ + tr.χ * *     | (d) |
| c) At Leesville field coupons. |
| 1 B 6 MAT χ + F + χ + tr.χ * *     | 1-c (a) |
| 1 B 15 MAT F + χ + χ + tr.χ *     | (b) |
| 2 B 1 MAT AM | (c) |
| 2 B 3 MAT F + AM | (d) |
| 2 B 1 YAT F + AM | (e) |
| At Leesville on location. |
| 3 B 2 YAT AM + F | (f) |
| 3 B 2 YAT AM + tr.F + 1YRT | (g) |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>3</td>
<td>MAT</td>
<td>F</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ferrihydrite (lab spn.)</td>
<td></td>
<td>F</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>MAT</td>
<td>F + AM + tr. $\gamma$ *</td>
</tr>
<tr>
<td>6</td>
<td>18</td>
<td>MAT</td>
<td>am.$\delta$ + $\gamma$</td>
</tr>
</tbody>
</table>

(h) (i) (j) (k)
FIGURE 2.3.1-a

IR absorption patterns of rusts formed on wire brushed cleaned weathering steel surfaces in bridges at Luling, La. and Doullut Canal, Empire, La.
FIGURE 2.3.1-b

IR absorption patterns of rusts formed on wire-brushed cleaned weathering steel surfaces treated with 10% Tannic Acid solution in the Doullut Canal bridge at Empire, La.
FIGURE 2.3.1-9

Absorption patterns formed on weathering steel panels (A588 Grade B) sand blast cleaned and treated with 25% Phosphoric Acid and Benzoic Acid
Table 2.3.2 Transformations of $\beta$-FeOOH ($\beta$)

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Time</th>
<th>Phases present</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>63 hrs</td>
<td>Pure $\beta$-FeOOH</td>
<td>No discernible change in the IR pattern</td>
</tr>
<tr>
<td>75°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150°C</td>
<td>30 hrs</td>
<td>$\beta$ + traces of $\chi$-FeOOH.H.O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>65 hrs</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>23 hrs</td>
<td>$\beta$-FeOOH (am)</td>
<td></td>
</tr>
<tr>
<td>180°C</td>
<td>70 hrs</td>
<td>$\beta$ starting to transform to $\chi$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>190°C</td>
<td>17 hrs</td>
<td>Incompletely Crystallized $\beta$-FeOOH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>23 hrs</td>
<td>traces of $\chi$ (am)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>99 hrs</td>
<td>Complete transformation to $\chi$</td>
<td>Mostly Crystalline</td>
</tr>
<tr>
<td></td>
<td>381 hrs</td>
<td>as above</td>
<td>Tendency for the form</td>
</tr>
<tr>
<td></td>
<td>780 hrs</td>
<td>$\chi$ (am)</td>
<td>Tendency for the form</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>to become more amorphous</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>This form is still stable during all these bakings.</td>
</tr>
<tr>
<td>200°C</td>
<td>42 hrs</td>
<td>Mixture of $\chi$ + $\alpha$-Fe$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>67 hrs</td>
<td>as above</td>
<td></td>
</tr>
<tr>
<td></td>
<td>95 hrs</td>
<td>$\alpha$-Fe$_2$O$_3$ + tr.$\chi$</td>
<td></td>
</tr>
</tbody>
</table>
305 hrs The above mixture pattern persisting to this baking time

\[ \begin{align*}
\text{230} & \text{ C} & 2 \text{ hrs} & \beta + \beta - \text{Fe}_3 \text{O}_2 \\
& & 5 \text{ hrs} & \text{Complete to } \alpha - \text{Fe}_3 \text{O}_2 \text{ (am)} \\
& & & \text{Not well crystallized}
\end{align*} \]

\[ \begin{align*}
\text{500} & \text{ C} & 4 \text{ hrs} & \text{Complete to } \alpha - \text{Fe}_3 \text{O}_2 \text{ (cryst.)} \\
& & & \text{Transformation is very fast. Well crystallized}
\end{align*} \]

b) In vacuum

\[ \begin{align*}
\text{170} & \text{ C} & 12 \text{ hrs} & \beta + \beta - \text{Fe}_2 \text{O}_3 \\
& & 19 \text{ hrs} & \beta - \text{Fe}_2 \text{O}_3 \text{ (am)} \\
& & 81 \text{ hrs} & \beta - \text{Fe}_2 \text{O}_3 \text{ (am)} \\
& & 274 \text{ hrs} & \beta - \text{Fe}_3 \text{O}_2 \text{ (am)} \\
& & & \text{Stable to 274 hrs at this temperature in vacuum}
\end{align*} \]

Initial bake at 170 C for 36 hrs + further bake at

\[ \begin{align*}
\text{190} & \text{ C} & 12 \text{ hrs} & \beta - \text{Fe}_3 \text{O}_2 \\
& & 168 \text{ hrs} & \beta - \text{Fe}_3 \text{O}_2 \text{ (am)} + \\
& & 216 \text{ hrs} & \text{more } \gamma \text{ (am)} \\
& & 252 \text{ hrs} & \text{only } \gamma \text{ (am)} \\
& & 354 \text{ hrs} & \text{more crystalline } \gamma \\
& & 441 \text{ hrs} & \text{as above} \\
& & 598 \text{ hrs} & \text{pure } \gamma \text{ Crystalline}
\end{align*} \]
\[ \beta = \beta^{-}\text{FeOOH}; \quad \chi = \chi^{-}\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}; \text{am} = \text{not well crystallized} \]

**Table 2.3.3 Transformations of \( \chi^{-}\text{FeOOH} (\chi) \)**

<table>
<thead>
<tr>
<th>Temp. C</th>
<th>Time</th>
<th>Phases present</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>24 hrs</td>
<td>( \chi^{-}\text{FeOOH} (\chi) ) + traces of ( \chi^{-}\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O} (\chi\text{am}) )</td>
<td>*</td>
</tr>
<tr>
<td>53 hrs</td>
<td>Significant amounts ( \chi\text{am} + \chi )</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>90 hrs</td>
<td>( \chi\text{am} ) + traces of ( \chi )</td>
<td>The amorphous form beginning to crystallize</td>
<td></td>
</tr>
<tr>
<td>120 hrs</td>
<td>( \chi\text{am} ) ( \rightarrow ) crystall. + traces of ( \chi )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>2.5 hrs</td>
<td>Complete to ( \chi\text{am} )</td>
<td></td>
</tr>
<tr>
<td>6.5 hrs</td>
<td>( \chi\text{am} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 hrs</td>
<td>Incompletely crystallized ( \alpha^{-}\text{Fe}_2\text{O}_3 + \text{traces of } \chi )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>81 hrs</td>
<td>( \chi\text{am} )</td>
<td>( \alpha^{-}\text{Fe}_2\text{O}_3 )</td>
<td>Not fully crystalline</td>
</tr>
<tr>
<td>400</td>
<td>4 hrs</td>
<td>( \alpha^{-}\text{Fe}_2\text{O}_3 )</td>
<td>Incompletely crystalline</td>
</tr>
<tr>
<td>24 hrs</td>
<td>( \alpha^{-}\text{Fe}_2\text{O}_3 )</td>
<td>Crystalline</td>
<td></td>
</tr>
<tr>
<td>60 hrs</td>
<td>( \alpha^{-}\text{Fe}_2\text{O}_3 )</td>
<td>Crystalline</td>
<td></td>
</tr>
</tbody>
</table>
b) in vacuum at 200 C

<table>
<thead>
<tr>
<th>time (hrs)</th>
<th>transformations</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>mostly transformed to amorphous (-\text{Fe O}_{2.3})</td>
</tr>
<tr>
<td>342</td>
<td>more of the same phase</td>
</tr>
<tr>
<td>495</td>
<td>()</td>
</tr>
<tr>
<td>676</td>
<td>dominant (-\text{Fe O}_{2.3}) but appearing clearly (-1)</td>
</tr>
</tbody>
</table>

at 905 cm
FIGURE 2.3.2-a.
FIGURE 2.3.2-b
FIGURE 2.3.2-c
FIGURE 2.3.3
FIGURE 234
Fig. 2.3.6. X-Ray pattern of two different preparations of β-FeOOH
Fig. 2.3.7. Transformations of $\kappa$-FeOOH in vacuum.

a) 0 hrs., b) 120 hrs., c) 342 hrs.,
d) 495 hrs., e) 676 hrs. at 200 C
Fig. 2.3.5. SEM micrographs of a) \( \alpha \)-FeOOH b) \( \beta \)-FeOOH
CAPTIONS TO FIGURES

Figure 2.3.2-a
Transformations of β-FeOOH in air at different temperatures
a) Pure β-FeOOH.

b) 3.5 hrs. at 75 C.

c) 63 hrs. at 75 C.

d) 30 hrs. at 150 C.

e) 65 hrs. at 150 C.

f) 70 hrs. at 180 C.

Figure 2.3.2-b
Transformations of β-FeOOH at 190 C

a) 17 hrs.

b) 169 hrs.

c) 381 hrs.

d) 780 hrs.

Figure 2.3.2-c
Transformations of β-FeOOH in air at different temperatures

a) 42 hrs. at 200 C.

b) 95 hrs. at 200 C.

c) 2 hrs. at 230 C.

d) 5 hrs. at 230 C.

e) 4 hrs. at 500 C.
Figure 2.3.3

Transformations of \( \beta \)-FeOOH in vacuum at different temperatures

a) Pure \( \beta \)-FeOOH.

b) 12 hrs. at 170 C.

c) 25 hrs. at 170 C.

d) 36 hrs. at 170 C.

e) 168 hrs. at 190 C.

f) 453 hrs. at 190 C.

g) 598 hrs. at 190 C.

Figure 2.3.4

Transformations of \( \chi \)-FeOOH in air at different temperatures

a) Pure \( \chi \)-FeOOH.

b) 53 hrs. at 100 C.

c) 120 hrs. at 100 C.

d) 2.5 hrs. at 300 C.

e) 11 hrs. at 300 C.

f) 45 hrs. at 300 C.

g) 4 hrs. at 400 C.

h) 24 hrs. at 400 C.
CONCLUSIONS

Mechanisms by electrochemical testing

1. Potentiostatic testing of weathering steel, at constant potentials in the vicinity of the open circuit potential, is well suited for the simulation of atmospheric corrosion. This is evidenced by the similar corrosion products obtained at the beginning of field exposure and potentiostatic tests.

2. The corrosion of weathering steel under the above mentioned testing conditions, consists of two distinct stages; a) dissolution, b) corrosion in the presence of oxide-hydroxide film.

3. The elementary ionization of the steel takes place by the adsorption of chloride ions to the steel surface, the formation of iron-chloro complexes and finally the hydrolysis of these to release the ferrous ion. The reaction sequence is given by the eqns. [22]-[24]. This mechanism was suggested by the determination of Tafel slopes for the reaction by potentiodynamic testing.

4. The adsorption of chloride ions to the steel surface, depends linearly on the magnitude of the displacement of the constant potential from the open circuit potential of the steel. This relationship is obeyed until saturation coverage of the surface by chloride ions, reached at a concentration of ~ 5% NaCl.

5. All measured parameters of the potentiostatic test
reach steady-state values at approximately the same time. Visual observation has shown that this stabilization is associated with the formation of oxide - hydroxide films of iron.

6. The magnitude of the potential shift can be accounted for by the diffusion potential of a membrane system for which the corrosion precipitate is a double layered membrane. This quantity arises from the diffusion of \( \text{Cl}^2\) ions inwards from the bulk solution, and \( \text{Fe}^{2+} \) outwards from the base metal.

7. Weathering steel corrodes in 25% phosphoric acid according to the Bockris mechanism of dissolution. The metal passivates slightly at a potential of \(~ -150 \text{ mV} \) vs. SCE forming a thin passive layer, the nature of which depends on the availability of oxygen.

8. The surface application of 25% phosphoric acid does not induce passivation on the weathering steel. The corrosion behaviour in this case is similar to that of bare weathering steel in the same salt solution. The corrosion products obtained are also identical; lepidocrocite in the presence of oxygen, and the amorphous form termed the amorphous mix(Am), in the absence of oxygen, similar to the atmospheric exposure tests.

9. The steady-state corrosion currents for inhibited weathering steel is approximately one order of magnitude lower than that for the uninhibited steel, the negative
shift in the rest potential is also considerably smaller. The reduction in corrosion rates is suggested to be due to the formation of bipolar precipitate films that have phosphate ions from solution adsorbed on them. The bipolarity of rust layers are predicted to be gradually destroyed by the substitution of adsorbed phosphate ions by chloride ions from the solution resulting in further corrosion and phase transition (which is indeed the case in field exposure testing).

10. Results from surface treatments of both coupons and bridge surface locations show that atmospheric rusting on weathering steels in sheltered locations starts off with the amorphous mix (AM) and, depending on the surface treatment, forms $\gamma$ and $\delta$-FeOOH in their amorphous forms.

11. The transformation sequence can be summarized for the majority of the treatments and bridges as:

$$\text{AM} \rightarrow \gamma + \delta - \text{FeOOH (am)} \rightarrow (\gamma + \delta) \rightarrow \delta + \gamma^*$$

12. The above sequence is only rarely disrupted to contain intermediates ferrihydrite (F) and $\gamma$-Fe$_2$O$_3$H$_2$O ($\gamma$) for specific bridges:

<table>
<thead>
<tr>
<th>Phases at the start of exposure</th>
<th>Final phases after 18 months of exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR, LV</td>
<td>AM $\rightarrow$ F $\rightarrow$ F + $\gamma^<em>$ $\rightarrow$ (F + $\delta$) + $\gamma^</em>$ (or AM + F)</td>
</tr>
<tr>
<td>LU</td>
<td>AM $\rightarrow$ $\gamma$(am) + AM $\rightarrow$ ($\gamma$ + $\delta$) + $\gamma^*$</td>
</tr>
</tbody>
</table>

13. The ferrihydrite would seem to occur exclusively in
the rural area bridges due to prevailing alkaline conditions and high concentrations of Ca and Si that may stabilize this phase.

14. $\chi$-Fe$_2$O$_3$H$_2$O occurs only at the intermediate stages of atmospheric rusting and gets converted probably to $\delta$-FeOOH. The occurrence of this phase may be connected with high chloride contents or high relative humidities and corrosion rates as it was found only at bridges located very close to the ocean.

15. All the chemical treatments slow down the rate of atmospheric corrosion and favor the stabilization of amorphous phases such as AM and amorphous forms of $\chi$* and $\delta$.

16. Infrared technique is demonstrably ideally suited for analysis of complex mixtures of atmospheric corrosion products that may be difficult to distinguish using other techniques. Infrared spectroscopy can also determine the time-wise development of phases within the atmospheric rust layer and point out the sequences of transformations by the progressive dominance of specific oxides and hydroxides of iron.

17. The $\delta$-fraction identified might include also some small amounts of $\chi$-FeOOH, since the IR absorption spectrum of coincides with that of . However, the powdery and flake-type rusts collected from several locations on the bridges show prevalence of in overwhelming quantities and $\alpha$-FeOOH seems to form only under highly alkaline conditions.
Thus, the stable final rust might be judged to contain only crystalline or amorphous \( \gamma \)-FeOOH and \( \alpha \)-FeOOH.

18. Lepidocrocite (\( \gamma \)-FeOOH) transforms to haematite in air through the intermediate \( \gamma \)-FeO\(.\)\( \cdot \)\( \text{H}_2\)O at the optimum temperature of 300°C.

19. Akagaenite (\( \beta \)-FeOOH) transforms to haematite through the intermediates \( \beta \)-FeO \(2\) and \( \gamma \)-FeO \(2\) \(\cdot\)\( \text{H}_2\)O both in vacuum and air in that order. The most suitable temperatures to study these transformations were 170°C for the vacuum and 190°C for the air transformations.

20. The intermediate phases are found to become more disordered or amorphous before they transform to the next phase.

21. \( \gamma \)-Fe\(2\)O\(3\) \(\cdot\)\( \text{H}_2\)O emerges as an important transient oxide-hydroxide and might have implications in furthering our understanding of atmospheric rusting mechanisms and phase transformations involving topotactic reactions.

22. Infrared spectroscopy is proven to be a powerful tool in following accurately the transformations of rust phases and to investigate the role of various forms of water in the structures of rust phases also.

**Recommendations for further study**

a) Dissolution mechanisms: The critical importance on the dissolution process of the complexation of chloride ions with iron was once again demonstrated. For a better elucidation of the initial stages of the corrosion process in the
presence of chloride ions, the precise stoichiometry and stability of these iron-chloro complexes would have to be determined. This could be done using a suitable spectrochemical technique in a manner similar to which differential pulse polarography was used in this study.

b) The significance of water in its many forms in the structures of oxide-hydroxide films was mentioned earlier. Infrared spectroscopy used in this study was necessarily an ex-situ technique due the nature of specimen preparation. Although infrared spectroscopy yields information on the forms of water in the rust layers, an in-situ technique that could characterize the corroding surface as dissolution and film formation take place would be invaluable. Reflection FT-IR spectroscopy or photo acoustic spectroscopy have been used in this type of studies.

c) The sensitivity of the polarographic technique could also be improved by a smaller electrochemical cell, thus greater concentrations, and a design that would allow sampling from the immediate vicinity of the working electrode to gain a better handle on the parameters studied at the immediate vicinity of the corroding anode.

d) Texture studies would be helpful to characterize the membrane films formed.
REFERENCES

15. Mikhailovsky, Y.N., Agafanov, H.B., Sanko, V.A.,
   Moscow, 1940.
42. Hoar, T.P., Hurlen, T., ibid.,
63. Chin, R.J., Nobe, K., ibid., 119, 1457 (1972).
64. Asakura, S., Nobe, K., ibid., 118, 19 (1971).
70. Dray, S., Sollner, K., Biochim. Biophys. Acta,
21,126(1956).
19,199(1979).
100,203(1953).
98,363(1951).
81. Bond, A., Modern Polarographic Methods in Analytical
82. Delahay,P., New Instrumental Methods in Electro-
chemistry, Wiley Interscience, N.Y., 1954.
83. Bard, A.J., Faulkner, L.R., Electrochemical Methods,
(1964), and 37,1634(1965).


131. Ozdemir, O. and Banerjee, K., Geo. Res. Lett. 11, 161
147. Raman, A., Paper (vi) in the IR series given in ref. 151.
152. A. Raman and B. Kuban, paper (iv) in the IR series, given in ref. 151.
APPENDIX

Average section thickness losses obtained from direct measurements at various locations in bridge spans in Louisiana and Texas

<table>
<thead>
<tr>
<th>Bridge Locations</th>
<th>Average Section Thickness Losses, mils/year +</th>
<th>Exterior vertical surfaces</th>
<th>Interior walls, horizontal and inclined faces</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ZONE 1: Mild, rural atmosphere</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boeuf river (BR)</td>
<td>about 1</td>
<td>inconclusive</td>
<td></td>
</tr>
<tr>
<td>Leesville (LV)</td>
<td>inconclusive</td>
<td>inconclusive</td>
<td></td>
</tr>
<tr>
<td><strong>Average:</strong></td>
<td>about 1</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td><strong>Estimate from field coupon data</strong></td>
<td>about 0.2</td>
<td>about 0.5</td>
<td></td>
</tr>
</tbody>
</table>

| **ZONE 2: Medium severe, industrial, near coastal atmosphere** |
| Forked Island (FI) | 2-2.5 | inconclusive |
| Gibbstown (GT)     | 2-3   | 2-4          |
| Luling (LU)- (approach span) | 2-3 | 2-3          |
| Larose (LR)        | inconclusive | 2-3 |
| **Average:**       | 2-3   | 2-4          |
| **Estimate from field coupon data** | about 1 | 1-1.5 |
| **From pitting data** | ---- | 2-4* |

| **ZONE 3: Severe, near marine atmosphere, close to Gulf coast** |
| High Island (HI)  | 3     | 4-5          |
| Doullut Canal (DC)| 3     | 3-4          |
| Luling (LU)- Main Span | 1.5-2 | 4-5          |
| **Average:**      | 3     | 3-5          |
| **Estimate from field coupon data** | 1-2   | 1.5-2        |
| **From pitting data** | ---- | 2-5*        |

* Conservative estimates from average and maximum pit depths measured. The losses could be higher than these values since some of the metal in the pitted area is also being uniformly corroded off. Thus the maximum values could be higher by one or two mils in selected localized areas of attack.

+ Multiply the values by 25 to convert to μm/year.
VITA

Mehmet Baha Kuban was born July 12, 1958 in Istanbul to Doğan and Sabiha. He obtained his high school diploma from Istanbul Anadolu Lisesi in 1976, B.Sc. from the University Manchester, U.K. in 1981 from the Department of Metallurgy. He later obtained his M.A.Sc. from the Metallurgical Engineering Department, the University of British Columbia in 1983. He came to Louisiana State University to pursue a Ph.D. in the interdisciplinary program of Engineering Science in 1983.
Candidate: Mr. Mehmet Baha KUBAN

Major Field: Engineering Science

Title of Dissertation: Mechanisms of the Atmospheric Corrosion of Weathering Steel

Approved:

[Signature]
Major Professor and Chairman

[Signature]
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signature]
Robert J. Gale

[Signature]
John C. Courtney

[Signature]
[Signature]
[Signature]

Date of Examination:

September 12, 1986