European Federation of
Corrosion Publications
Number 52

Progress in corrosion – The first 50 years of the EFC

Edited by
P. McIntyre & J. Vogelsang

The Institute of Materials, Minerals & Mining

EFC
EUROPEAN FEDERATION OF CORROSION
FÉDÉRATION EUROPÉENNE DE LA CORROSION
EUROPÄISCHE FÖDERATION KORROSION

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European Federation of Corrosion (EFC) publications: Series introduction

The European Federation of Corrosion (EFC), incorporated in Belgium, was founded in 1955 with the purpose of promoting European cooperation in the fields of research into corrosion and corrosion prevention.

Membership of the EFC is based upon participation by corrosion societies and committees in technical Working Parties. Member societies appoint delegates to Working Parties, whose membership is expanded by personal corresponding membership.

The activities of the Working Parties cover corrosion topics associated with inhibition, education, reinforcement in concrete, microbial effects, hot gases and combustion products, environment-sensitive fracture, marine environments, refineries, surface science, physico-chemical methods of measurement, the nuclear industry, the automotive industry, computer-based information systems, coatings, tribocorrosion and the oil and gas industry. Working Parties and Task Forces on other topics are established as required.

The Working Parties function in various ways, e.g. by preparing reports, organising symposia, conducting intensive courses and producing instructional material, including films. The activities of Working Parties are coordinated, through a Science and Technology Advisory Committee, by the Scientific Secretary. The administration of the EFC is handled by three Secretariats: DECHEMA e.V. in Germany, the Fédération Française pour les sciences de la Chimie (formely Société de Chimie Industrielle) in France, and The Institute of Materials, Minerals and Mining in the UK. These three Secretariats meet at the Board of Administrators of the EFC. There is an annual General Assembly at which delegates from all member societies meet to determine and approve EFC policy. News of EFC activities, forthcoming conferences, courses, etc., is published in a range of accredited corrosion and certain other journals throughout Europe. More detailed descriptions of activities are given in a Newsletter prepared by the Scientific Secretary.

The output of the EFC takes various forms. Papers on particular topics, e.g. reviews or results of experimental work, may be published in scientific and technical journals in one or more countries in Europe. Conference proceedings are often published by the organisation responsible for the conference.

In 1987 the, then, Institute of Metals was appointed as the official EFC publisher. Although the arrangement is non-exclusive and other routes for publication are still available, it is expected that the Working Parties of the EFC will use The Institute of Materials, Minerals and Mining for publication of reports, proceedings, etc., wherever possible.

The name of The Institute of Metals was changed to The Institute of Materials (IoM) on 1 January 1992 and to The Institute of Materials, Minerals and Mining with effect from 26 June 2002. The series is now published by Maney Publishing on behalf of The Institute of Materials, Minerals and Mining.

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* indicates volume out of print

1 **Corrosion in the nuclear industry**
*Prepared by Working Party 4 on Nuclear Corrosion**

2 **Practical corrosion principles**
*Prepared by Working Party 7 on Corrosion Education**

3 **General guidelines for corrosion testing of materials for marine applications**
*Prepared by Working Party 9 on Marine Corrosion**

4 **Guidelines on electrochemical corrosion measurements**
Prepared by Working Party 8 on Physico-Chemical Methods of Corrosion Testing

5 **Illustrated case histories of marine corrosion**
Prepared by Working Party 9 on Marine Corrosion

6 **Corrosion education manual**
Prepared by Working Party 7 on Corrosion Education

7 **Corrosion problems related to nuclear waste disposal**
Prepared by Working Party 4 on Nuclear Corrosion

8 **Microbial corrosion**
*Prepared by Working Party 10 on Microbial Corrosion**

9 **Microbiological degradation of materials and methods of protection**
Prepared by Working Party 10 on Microbial Corrosion

10 **Marine corrosion of stainless steels: chlorination and microbial effects**
Prepared by Working Party 9 on Marine Corrosion

11 **Corrosion inhibitors**
*Prepared by the Working Party on Inhibitors**

12 **Modifications of passive films**
*Prepared by Working Party 6 on Surface Science**

13 **Predicting CO_2 corrosion in the oil and gas industry**
*Prepared by Working Party 13 on Corrosion in Oil and Gas Production**

14 **Guidelines for methods of testing and research in high temperature corrosion**
Prepared by Working Party 3 on Corrosion by Hot Gases and Combustion Products

15 **Microbial corrosion: Proceedings of the 3rd International EFC Workshop**
Prepared by Working Party 10 on Microbial Corrosion

16 **Guidelines on materials requirements for carbon and low alloy steels for H_2S-containing environments in oil and gas production (3rd Edition)**
Prepared by Working Party 13 on Corrosion in Oil and Gas Production

17 **Corrosion resistant alloys for oil and gas production: guidance on general requirements and test methods for H_2S service**
Prepared by Working Party 13 on Corrosion in Oil and Gas Production

18 **Stainless steel in concrete: state of the art report**
Prepared by Working Party 11 on Corrosion of Steel in Concrete

19 **Sea water corrosion of stainless steels: mechanisms and experiences**
Prepared by Working Party 9 on Marine Corrosion and Working Party 10 on Microbial Corrosion

20 **Organic and inorganic coatings for corrosion prevention: research and experiences**
Papers from EUROCORR '96

21 **Corrosion-deformation interactions**
CDI '96 in conjunction with EUROCORR '96

22 **Aspects of microbially induced corrosion**
Papers from EUROCORR '96 and EFC Working Party 10 on Microbial Corrosion

23 **CO_2 corrosion control in oil and gas production: design considerations**
Prepared by Working Party 13 on Corrosion in Oil and Gas Production

24 **Electrochemical rehabilitation methods for reinforced concrete structures: a state of the art report**
Prepared by Working Party 11 on Corrosion of Steel in Concrete

25 **Corrosion of reinforcement in concrete: monitoring, prevention and rehabilitation**
Papers from EUROCORR '97

26 **Advances in corrosion control and materials in oil and gas production**
Papers from EUROCORR '97 and EUROCORR '98

27 **Cyclic oxidation of high temperature materials**
Proceedings of an EFC Workshop, Frankfurt/Main, 1999

28 **Electrochemical approach to selected corrosion and corrosion control**
Papers from the 50th ISE Meeting, Pavia, 1999

29 **Microbial corrosion: proceedings of the 4th International EFC Workshop**
Prepared by the Working Party on Microbial Corrosion

30 **Survey of literature on crevice corrosion (1979–1998): mechanisms, test methods and results, practical experience, protective measures and monitoring**
Prepared by F. P. Ijsseling and Working Party 9 on Marine Corrosion

31 **Corrosion of reinforcement in concrete: corrosion mechanisms and corrosion protection**
Papers from EUROCORR '99 and Working Party 11 on Corrosion of Steel in Concrete

32 **Guidelines for the compilation of corrosion cost data and for the calculation of the life cycle cost of corrosion: a working party report**
Prepared by Working Party 13 on Corrosion in Oil and Gas Production

33 **Marine corrosion of stainless steels: testing, selection, experience, protection and monitoring**
Edited by D. Féron on behalf of Working Party 9 on Marine Corrosion

34 **Lifetime modelling of high temperature corrosion processes**
Proceedings of an EFC Workshop 2001 Edited by M. Schütze, W. J. Quadakkers and J. R. Nicholls

35 **Corrosion inhibitors for steel in concrete**
Prepared by B. Elsener with support from a Task Group of Working Party 11 on Corrosion of Steel in Concrete

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Edited by D. Féron on behalf of Working Party 4 on Nuclear Corrosion

37 **Test methods for assessing the susceptibility of prestressing steels to hydrogen induced stress corrosion cracking**
By B. Isecke on behalf of Working Party 11 on Corrosion of Steel in Concrete

38 **Corrosion of reinforcement in concrete: mechanisms, monitoring, inhibitors and rehabilitation techniques**[#]
Edited by M. Raupach, B. Elsener, R. Polder and J. Mietz on behalf of Working Party 11 on Corrosion of Steel in Concrete

39 **The use of corrosion inhibitors in oil and gas production**
Edited by J. W. Palmer, W. Hedges and J. L. Dawson on behalf of Working Party 13 on Corrosion in Oil and Gas Production

40 **Control of corrosion in cooling waters**
Edited by J. D. Harston and F. Ropital on behalf of Working Party 15 on Corrosion in the Refinery Industry

41 **Metal dusting, carburisation and nitridation**[#]
Edited by H. Grabke and M. Schütze on behalf of Working Party 3 on Corrosion by Hot Gases and Combustion Products

42 **Corrosion in refineries**[#]
Edited by J. D. Harston and F. Ropital on behalf of Working Party 15 on Corrosion in the Refinery Industry

43 **The electrochemistry and characteristics of embeddable reference electrodes for concrete**[#]
Prepared by R. Myrdal on behalf of Working Party 11 on Corrosion of Steel in Concrete

44 **The use of electrochemical scanning tunnelling microscopy (EC-STM) in corrosion analysis: reference material and procedural guidelines#**
Prepared by R. Lindström, V. Maurice, L. Klein and P. Marcus on behalf of Working Party 6 on Surface Science

45 **Local probe techniques for corrosion research#**
Edited by R. Oltra on behalf of Working Party 8 on Physico-Chemical Methods of Corrosion Testing

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Edited by J. D. Harston and F. Ropital on behalf of Working Party 15 on Corrosion in the Refinery Industry

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Edited by M. Schütze and W. Quadakkers on behalf of Working Party 3 on Corrosion by Hot Gases and Combustion Products

48 **Corrosion of metallic heritage artefacts: investigation, conservation and prediction of long term behaviour#**
Edited by P. Dillmann, G. Béranger, P. Piccardo and H. Matthiesen on behalf of Working Party 4 on Nuclear Corrosion

49 **Electrochemistry in light water reactors: reference electrodes, measurement, corrosion and tribocorrosion#**
Edited by R.-W. Bosch, D. Féron and J.-P. Celis on behalf of Working Party 4 on Nuclear Corrosion

50 **Corrosion behaviour and protection of copper and aluminium alloys in seawater#**
Edited by D. Féron on behalf of Working Party 9 on Marine Corrosion

51 **Corrosion issues in light water reactors: stress corrosion cracking#**
Edited by D. Féron and J-M. Olive on behalf of Working Party 4 on Nuclear Corrosion

52 **Progress in Corrosion – The first 50 years of the EFC**
Edited by P. McIntyre and J. Vogelsang on behalf of the EFC Science and Technology Advisory Committee

53 **Standardisation of thermal cycling exposure testing#**
Edited by M. Schütze and M. Malessa on behalf of Working Party 3 on Corrosion by Hot Gases and Combustion Products

54 **Innovative pre-treatment techniques to prevent corrosion of metallic surfaces#**
Edited by L. Fedrizzi, H. Terryn and A. Simões on behalf of Working Party 14 on Coatings

55 **Corrosion-under-insulation (CUI) guidelines#**
Prepared by S. Winnik on behalf of Working Party 13 on Corrosion in Oil and Gas Production and Working Party 15 on Corrosion in the Refinery Industry

All volumes (except those marked with #) are available from Maney Publishing or its North American distributor. See http://maney.co.uk/index.php/series/efc_series/ Volumes marked with # were published on behalf of Maney by Woodhead Publishing, from whom they should be ordered. See www.woodheadpublishing.com

Preface

The European Federation of Corrosion (EFC) is an association of societies with interests in corrosion. It has now been in existence for over fifty years, a period that has seen tremendous advances in the understanding and control of corrosion processes.

Originally formed with the objective of fostering the work of its member societies, the EFC soon identified the need to establish working parties to facilitate the coordination and planning of work on particular aspects of corrosion. To begin with, four working parties were formed, on Inhibitors, Protection of Steel Structures, Corrosion by Hot Gases and Combustion Products, and Nuclear Corrosion. Over the years, the number has increased steadily and there are now seventeen active working parties with another currently in the process of being formed. Jointly, they deal with all of the most important facets of corrosion, protection and education.

In order to mark the golden anniversary of the EFC in 2005, the Science and Technology Advisory Committee resolved to commence work on a new volume in the EFC Series to document the history of the Federation and some of the ways in which it had contributed to the general advancement of the science of corrosion and the protection of materials through international cooperation, transfer of knowledge and education. It was suggested that an article prepared by the EFC Scientific Secretary for the anniversary edition of the EFC Newsletter could be used as the introductory chapter. In addition, the working party chairmen were invited to contribute to the book and, despite their heavy work loads and other commitments, the majority have found time to do so, sometimes with help from their predecessors. It was proposed that they should address developments in their respective fields since the EFC was formed, highlighting the contributions made by their working parties. Otherwise they were given *carte-blanche* with regard to their treatment of the task.

The result is a unique survey of progress in the field of corrosion over the past half-century, culminating in the current state-of-the-art, by some of the most talented exponents of its science and technology.

Jörg Vogelsang
Past Chairman, EFC Science and Technology
Advisory Committee

Paul McIntyre
EFC Scientific Secretary

1

Introductory overview of the European Federation of Corrosion

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1.1 Introduction

The European Federation of Corrosion (EFC) was founded over 50 years ago, having been proposed at a meeting of the European Convention of Chemical Technology (ECCT) held in Frankfurt on 19 May 1955. The meeting was chaired by Professor Dr-Ing., Dr.rer.nat h.c. Karl Winnacker, Chairman of DECHEMA. The ECCT consisted of 31 technical and scientific societies from nine different countries (Table 1.1), including Austria (five societies), France (nine), Germany (seven), Italy (two), Yugoslavia (one), Luxembourg (one), Spain (one), Sweden (one) and Switzerland (four). Each society was wholly or partially concerned with the field of corrosion, and from the outset the object of the EFC was to foster the work of its member societies. Over the intervening half-century, the EFC has established itself as a leading international organisation, which has developed through international cooperation, transfer of knowledge and education [1]. Its activity has grown to encompass virtually all aspects of corrosion.

The EFC currently has 31 member societies, now distributed between 25 different European countries, including a number in central and eastern Europe. Its success is a great tribute to all who have given freely of their time in the interests of promoting cooperation in the field of research.

1.2 Early days of the EFC (1955–1984)

The EFC is a non-profit-making association of European societies with interests in corrosion that was established with the aim of advancing the science of the corrosion and protection of materials by promoting cooperation in Europe and collaboration internationally. It has never had individuals as members, with the exception of a very small number of quite exceptional people to whom Honorary Membership of the EFC has been extended (Fig. 1.1 and Table 1.2).

Following its formation in May 1955, the number of member societies grew quickly. By the beginning of 1956, the initial membership of 32 societies from nine countries had grown to 40 [2], with the addition of societies from four new member countries (Finland, Greece, Norway and Portugal) as well as others from France, Spain, Yugoslavia and Switzerland. By the time of its tenth anniversary, in 1965, membership had grown to 61 societies (plus six corresponding members) [3] and the

Table 1.1 The original founder societies of the EFC

Asociación Nacional de Quimicos de España	Spain
Association pour l'Encouragement à la Recherche Aéronautique	France
Association Française des Chimistes des Industries du Cuir	France
Association Française des Techniciens des Peintures et Vernis	France
Association des Chimistes et Ingénieurs de Sucrerie, de Distillerie et des Industries Agricoles de France et des Colonies	France
Association des Ingénieurs en Anti-Corrosion	France
Associazione Italiana di Metallurgia, Centro Corrosione	Italy
Association Luxembourgeoise des Ingénieurs Diplômés	Luxembourg
Association pour la Protection de Matériaux	Yugoslavia
Commissions per lo studio dei Fenomeni di Corrosions del Consiglio Nazionale delle Ricerche	Italy
DECHEMA Deutsche Gesellschaft für chemisches Apparatewesen	Germany
Deutsche Gesellschaft für Metallkunde	Germany
Deutscher Verein von Gas- und Wasserfachmännern	Germany
Eisenhütte Östereich Unterausschuss für Korrosionsfragen	Austria
Gesellschaft Deutscher Chemiker	Germany
Ingeniöravetenskapsakedemien, Korrosionsnamnd	Sweden
Österreichische Arbeitagemeinschaft für Korrosion	Austria
Österreichischer Ingenieur- und Architekten-Verein	Austria
Österreichischer Stahlbau-Verein	Austria
Société de Chimie Industrielle	France
Société des Ingénieurs Civils de France	France
Société Française de Microscopie Théorique et Appliquée	France
Société des Ingénieurs pour la France d'outre mer et des Pays exterieurs	France
Schiffbautechnische Gesellschaft	Germany
Schweizerischer Elektrotechnischer Verein	Switzerland
Schweizerischer Ingenieur- und Architekten-Verein	Switzerland
Schweizerischer Verband für die Materialprüfung der Technik	Switzerland
Schweizerischer Verein von Gas- und Wasserfachmännern	Switzerland
Verein Deutscher Eisenhüttenleute	Germany
Verein Deutscher Ingenieure	Germany
Verein Österreichischer Chemiker	Austria

EFC was able to claim representation in all western European countries (with the exception of Ireland), together with Czechoslovakia and Hungary.

When the EFC was first established, the administration was undertaken by an Executive Committee of six members representing France, Germany, Italy, Spain, Sweden and Switzerland, and a decision-making board consisting of the presidents of the member societies (or their delegates). No subscription charges for membership of the EFC were levied. The General Secretariat was established at two offices, at the Société de Chimie Industrielle in Paris and at DECHEMA in Frankfurt, and a Scientific Advisory Council was appointed to oversee technical matters. In those early days, the EFC focused its attention on supporting the work of its member societies by bringing about contact between specialists, encouraging and providing suggestions, and drawing attention to and increasing the effectiveness of the symposia staged by its member societies. It undertook no research work and did not organise regular symposia of its own. However, the Frankfurt office did prepare an Annual Report intended to bring about contact between specialists with common interests.

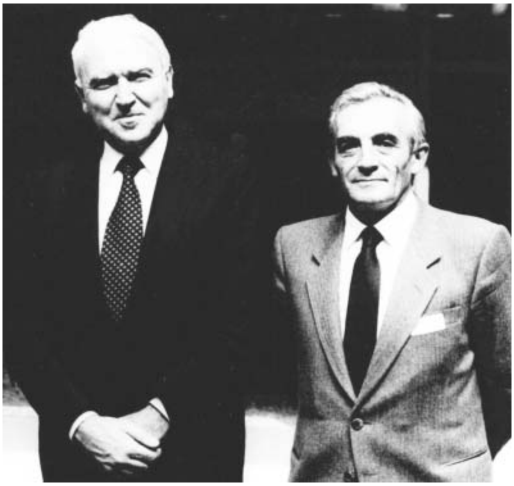
1.1 Hans Grabke (left) receives Honorary Membership of the EFC from Philippe Berge at EUROCORR 2001 in Riva del Garda

Table 1.2 Honorary members of the EFC

1989	Dr David Sharp	UK
1989	Dr-Ing. André L. Saboz	Switzerland
2001	Professor Hans J. Grabke	Germany
2003	Professor Giordano Trabanelli	Italy

In 1965, in order to fulfil its task more adequately, the EFC established a General Assembly composed of corrosion specialists, who were appointed by the member societies for 3-year periods, to replace the board, many of whose members were not specialists in corrosion. This measure provided greater stability and technical competence to the decision-making body of the EFC. By this time, the UK had become heavily involved in the EFC through the Society for Chemical Industry in London. It was represented on the Executive Committee, which now included eight countries, by Lieutenant Colonel F. J. Griffin, OBE. Members, whose names still resonate within the EFC, included Professor Dieter Behrens for Germany (Fig. 1.2) and Mr Hans Arup for the Scandinavian countries (Fig. 1.3). Professor Behrens is remembered for having done much to encourage the participation of central and eastern European countries in the EFC. The remaining five members of the 1965 Executive Committee were: G. Biva, Belgium; V. Carassiti, Italy; A. Ellefsen, France; P. Sulzer, Switzerland; and H. G. Zelders, The Netherlands.

Also in 1965, the Scientific Advisory Committee was reconstituted to give it more influence over the activities of the EFC. Its membership of 18 came from ten different countries and, among other well-known personalities, included Dr Ir. M. Pourbaix (Belgium, Fig. 1.4), Professor G. Chaudron (France), Professor H. Fischer (Germany) and Professor G. Biachi (Italy).



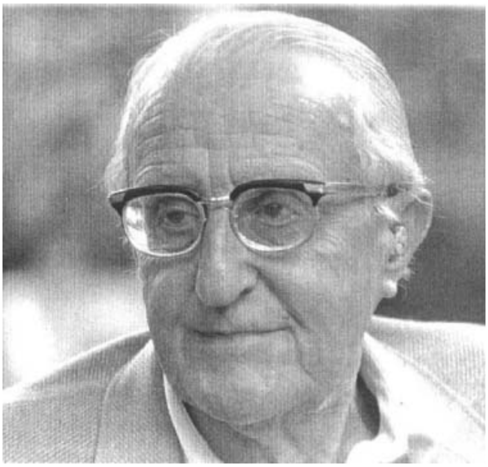
1.2 Two legendary EFC personalities, Professor Dieter Behrens, Germany (left) and Professor Giordano Trabanelli of Italy

1.3 Hans Arup (left) presents the European Corrosion Medal for 1991 to Dr Jos Weber of Sulzer Innotec, Switzerland

EFC working parties (WPs) were conceived during 1965 to facilitate the coordination and planning of work in specialised fields of corrosion in Europe. Top priority was given to the formation of WPs directed to the following topics:

- WP1 – Inhibitors
- WP2 – Protection of Steel Structures
- WP3 – Corrosion by Hot Gases and Combustion Products
- WP4 – Nuclear Corrosion

By 1976, 21 years after its formation [4], the EFC had 63 member societies in 19 countries and had successfully established nine active WPs, with chairmen as follows:



1.4 Marcel Pourbaix

- WP1 – Inhibitors; G. Trabanelli
- WP2 – Corrosion Protection of Steel Structures; R. Scimar
- WP3 – Corrosion by Hot Gases and Combustion Products; A. Rahmel
- WP4 – Nuclear Corrosion; H. Coriou
- WP5 – Stress Corrosion Test Methods; R. N. Parkins (Fig. 1.5)
- WP6 – Surface Condition Influence on Corrosion; J. Talbot
- WP7 – Corrosion Education; G. Svendenius
- WP8 – Physico-Chemical Methods of Corrosion Testing; R. Grauer
- WP9 – Marine Corrosion; H. Arup

During 1979, a feeling emerged within the EFC that although it had been in existence for 24 years, it had to a large extent been concerned with its own organisation and activities. Although these had achieved some far-reaching results, particularly with regard to publications, education and conferences, there was a desire

1.5 Redvers Parkins, first chairman of WP5 to bring the work of the EFC to the notice of a wider circle of interest in order to seek comments on its future development and activities. Therefore, two changes occurred.

First, it was decided to launch the EFC Newsletter, which has continued in production, in two different series, ever since (Fig. 1.6). The first series, of seven issues [5–11], appeared at irregular intervals between 1979 and 1990, and the second, of 14 issues [12–25], has appeared annually from August 1991 to date. The early issues were straightforward typewritten documents, without any illustrations, and sometimes as little as two pages in length. The post-1991 series has become more ambitious, with full colour illustrations since the year 2000, and sometimes running up to 32 pages in length.

Second, it was decided that the Science Advisory Committee of the EFC should organise major European conferences at regular intervals of about 2 or 3 years [5]. Hitherto, during the 21-year interval between the 1st European Corrosion Congress, in Paris (November 1956), and the 6th European Corrosion Congress, in London (September 1977), when it attracted an attendance of over 400, these events had taken place at irregular intervals.

In the 26 years since 1979, the EFC has organised 18 further major European corrosion conferences (see Table 1.3, which also provides details of forthcoming conferences up to and including EUROCORR 2008 in Moscow).

Prior to 1981, the EFC's corrosion conferences were always referred to as 'European Corrosion Congresses'. Then, in 1982, the name 'EUROCORR' was used for the first time. Between 1982 and 1993, the name alternated between 'European Corrosion Congress' (Fig. 1.7) and 'EUROCORR'. During the past decade,

EUROPEAN FEDERATION OF CORROSION. NEWSLETTER No. 1

The European Federation of Corrosion (EFC) is a non-profit-making association founded in 1955 with the objective of drawing together those concerned with corrosion and corrosion protection in the continent of Europe. Membership is therefore open to all European countries and is in no way related to membership of the European Economic Community (EEC).

Participation in the activities of the EEC is through membership of societies concerned with corrosion matters in the various countries. For example, in the United Kingdom these societies include the Society of Chemical Industry, the Institution of Corrosion Science and Technology, the Metals Society and the Institute of Metal Finishing. These organisations are represented on the National Council of Corrosion Societies which, in turn, appoints delegates to the committees of the EEC. Similar arrangements exist for other countries in the EFC and the member societies involved are listed in an Appendix to this Newsletter.

The technical aspects of EEC work are managed through a series of Working Parties (WP) that are concerned with various topics relating to the science and practice of corrosion and its prevention.

Overall guidance in the direction of the work of the EEC is provided by a Science Advisory Committee and an Executive Committee with responsibilities respectively for the scientific and business activities. The Science Advisory. Committee and Working Parties present reports on their activities to the General Assembly which will in future meet once every two years. This Assembly acts as the legislative body of the EEC, for example the establishment of a new Working Party requires the approval of this body. The General Assembly meets in a different country each year (UK in 1977, France in 1979, Germany in 1981) and the Chairman is always from the host country. He has the responsibility to present a report at the next General Assembly on corrosion work carried out within the member countries of the EFC during the period since the previous General Assembly. (The report prepared by the UK Chairman who retired in 1977 and which covers the period between the London and Paris General Assemblies will appear shortly in European corrosion journals e.g. the British Corrosion Journal in the UK.)

Number 14 - September 2004

EFC NEWSLETTER

FÉDÉRATION EUROPÉENNE DE LA CORROSION
EUROPEAN FEDERATION OF CORROSION
EUROPÄISCHE FÖDERATION KORROSION

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EUROCORR 2005

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EUROCORR 2005 takes place in Lisbon, capital of Portugal for more than 700 years. Organised by the Portuguese Society for Materials (SPM), EFC's newest Member Society, it will take place as EFC Event Number 273 on 4th - 8th September 2005. It will provide a forum for the international exchange of information about all aspects of corrosion and corrosion protection. The overall theme, to which all 17 EFC Working Parties will contribute, is **Corrosion Control for Sustainable Development**.

This landmark event coincides with the Golden Anniversary of the EFC, founded in 1955, and will feature special plenary lectures to mark the occasion. It will also be the first time that EUROCORR has been held in Portugal and an additional feature of EUROCORR 2005 will be a session on Corrosion Control in the Aeronautical Industry. Full details of the conference are available on its website: **http://www.eurocorr2005.org**

1

1.6 Evolution of the EFC Newsletter: 1st Series, No. 1 (1979); 2nd Series, No. 14 (2004)

Table 1.3. EFC European corrosion conferences

1956	1st European Corrosion Congress, Paris, France
1958	2nd European Corrosion Congress, Frankfurt am Main, Germany
1963	3rd European Corrosion Congress, Brussels, Belgium
1969	4th European Corrosion Congress, Amsterdam, The Netherlands
1973	5th European Corrosion Congress, Paris, France
1977	6th European Corrosion Congress, London, UK
1981	7th European Corrosion Congress, Mainz, Germany
1982	EUROCORR ’82, Budapest, Hungary
1985	8th European Corrosion Congress, Nice, France
1987	EUROCORR ’87, Karlsruhe, Germany
1988	EUROCORR ’88, Brighton, UK
1989	9th European Corrosion Congress, Utrecht, The Netherlands
1991	EUROCORR ’91, Budapest, Hungary
1992	EUROCORR ’92, Espoo, Finland
1993	10th European Corrosion Congress, Barcelona, Spain
1994	EUROCORR ’94, Bournemouth, UK
1996	EUROCORR ’96, Nice, France
1997	EUROCORR ’97, Trondheim, Norway
1998	EUROCORR ’98, Utrecht, The Netherlands
1999	EUROCORR ’99, Aachen, Germany
2000	EUROCORR 2000, London, UK
2001	EUROCORR 2001, Riva del Garda, Italy
2003	EUROCORR 2003, Budapest, Hungary
2004	EUROCORR 2004, Nice, France
2005	EUROCORR 2005, Lisbon, Portugal
2006	EUROCORR 2006, Maastricht, The Netherlands
2007	EUROCORR 2007, Freiburg, Germany (9–13 September 2007)
2008	EUROCORR 2008, Edinburgh, UK (7–11 September 2008)
2009	EUROCORR 2009, Nice, France (6–10 September 2009)
2010	EUROCORR 2010, Moscow, Russia (13–17 September)

1.7 Opening of the 10th European Corrosion Congress, Barcelona, 1993

'EUROCORR' has firmly established itself as the main annual event in the European corrosion calendar, the only exceptions to its yearly appearance being in years such as 2002, when there was a conflicting International Corrosion Congress in Granada.

In 1981, the General Assembly approved proposals to rename the Science Advisory Committee as the Science and Technology Advisory Committee (STAC), to highlight the new emphasis on industrial applications, and to establish technical sub-committees to ensure industrial input to the WPs [6]. It was also agreed that task forces (TFs) would be set up for a limited duration as and when necessary to deal with particular problems. However, it soon became apparent that the technical sub-committees were not really needed, since all requirements could be met by the WPs and TFs alone.

Another major development [7] was the decision to appoint an EFC scientific secretary to deal centrally with the scientific and technical aspects of the EFC's work, by developing and coordinating the activities of the STAC and the working parties. The scientific secretary reports to the STAC, and his activities include, among other things, the preparation and distribution of agendas, working papers and minutes for the STAC, the preparation of the EFC Newsletter for publication, and maintaining the register of EFC Event Numbers and Calendar of Events. Mr A. D. Mercer (Fig. 1.8) was appointed to this role in 1982, a position that he held until his retirement at the end of 1996, when he was succeeded by the present author.

1.3 Recent times (1984–2005)

The EFC acquired legal status in April 1984, when it became registered at the address of a Belgian member society (Branche Belge de la SCI) in Brussels [8]. On this occasion, the old EFC with its then 65 ordinary members from 20 European countries and 11 corresponding members from nine European countries and two overseas countries

1.8 Mr A. D. Mercer, EFC Scientific Secretary 1982–1996 was disbanded, although many of the societies decided to continue their membership in the new EFC. Statutes were prepared that identified four founding members:

- Branch Belge de la Société de Chimie Industrielle (Brussels)
- Société de Chimie Industrielle (Paris)
- DECHEMA (Frankfurt)
- Society of Chemical Industry (London) – superseded in 1986 by the then Institute of Metals, now The Institute of Materials, Minerals and Mining (London)

The three offices of the General Secretariat of the new EFC were now located at the offices of the founding members in Paris, Frankfurt and London, each of which was, to begin with, given responsibility for the member societies in its locale. These changes meant that the EFC was now free to enter into contractual arrangements (e.g. with the European Commission), could receive and make payments for research projects and publications, and could take legal action in its own name.

The old Executive Committee of the EFC was abandoned, and its role was taken over by a new Board of Administrators that included representatives nominated by each of the four founding member countries together with others from Denmark, Italy, Switzerland and The Netherlands.

The nine WPs of the new EFC in 1984 remained the same as they had been in 1976. However, things changed in October 1985, when the Chairman of WP2 on Corrosion and Protection of Steel Structures resigned and disbanded the group, due to waning interest among its members.

In January 1987, the number of WPs was restored to nine again when the inaugural meeting of the new WP10 on Microbial Corrosion took place in Trondheim [9], with Mr Kenneth Tiller (UK) as its chairman (Fig. 1.9).

Later in 1987, WP11 on Corrosion of Reinforcement in Concrete was formed under the chairmanship of Professor Bernd Isecke (Germany) [10].

1.9 Mr K. A. Tiller, first chairman of WP10

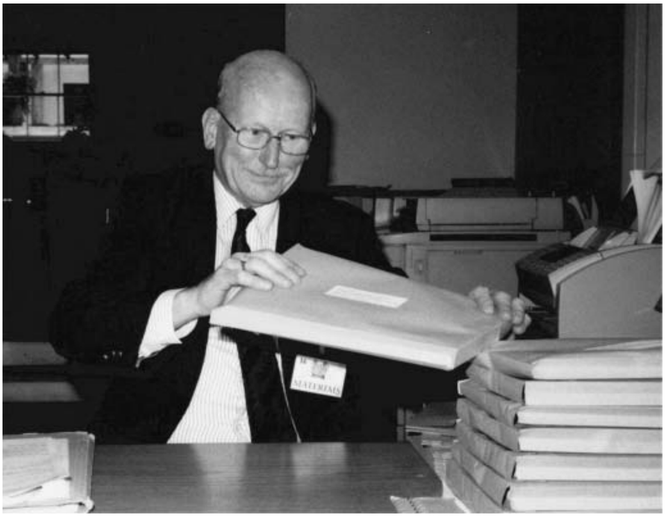
In 1988, another new working party, WP12 on Computer-Based Information Systems, under the chairmanship of Dr R. Deplanque (Germany), was ratified by the General Assembly [11], which was now composed of representatives from each of the member societies.

Further important changes in the administration of the EFC took place in 1988 when different responsibilities were identified for the three offices of the General Secretariat. Whereas these had previously shared responsibility for the member societies, the Frankfurt office was now given responsibility for membership, both of the EFC and of its WPs. At the same time, the Paris office became responsible both for the arrangement of meetings of the Board of Administrators and the General Assembly (including the preparation and distribution of agendas, working papers and minutes) and for all matters relating to the EFC awards. The London office became responsible for finance, and subsequently, in 1994, Dr Charles Booker (UK) (Fig. 1.10) was appointed as EFC honorary treasurer, a position that he held until 2005. The current treasurer is Mr Ray Milbank, whose appointment was approved by the General Assembly during EUROCORR 2006 in Maastricht.

In 1990, it was decided to open up participation in the EFC WPs to enable a wider range of interested persons to contribute to their activities. Although new participants were expected to belong to EFC member societies, this was no longer a mandatory requirement.

During 1991, proposals for a new WP on Corrosion in Oil and Gas Production arose from discussions among several EFC countries, and culminated in the formation of WP13, with Dr L. M. Smith (UK) as chairman.

A very significant development took place in June 1992, when the General Assembly appointed Mr C. J. Bijl (The Netherlands) (Fig. 1.11) as the first ever EFC president for a term of 2 years. This provided the EFC with an important representative for it and its policies, capable of providing leadership, and of providing continuity throughout his term of office by chairing meetings of the Board of Administrators and the General Assembly.



1.10 Charles Booker preparing items for despatch from the London office

1.11 Mr C. J. Bijl, first EFC president, 1993–1994

Since Mr Bijl left office at the end of 1994, there have been six other EFC presidents (Figs 1.12–1.15). Each president has contributed much in his own way to the success of the EFC during the past 14 years. In recent years, the president has been assisted by a small President's Task Force, which usually meets twice yearly during the intervals between Board of Administrators meetings to assist in drafting agendas and working papers.

Between 1993 and 2002, there was much activity concerned with the formation of new WPs. To begin with, in 1993, proposals were approved for a new WP, WP14 on Coatings, with Professor Dr Pier-Luigi Bonora (Italy) as its first chairman. Then, in 1996, another new WP, WP15 on Corrosion in the Refinery Industry, was approved by the EFC General Assembly in Nice, with Dr John Harston (UK) as its first

1.12 EFC presidents 1995–2001: Professor B. Isecke, 1995–96; Prof. P.-L. Bonora, 1997–99; Dr. J. P. Berge, 2000–2001

1.13 Mr D. Harrop: EFC president 2002–2003

1.14 Professor B. Linder: EFC president 2004–2005

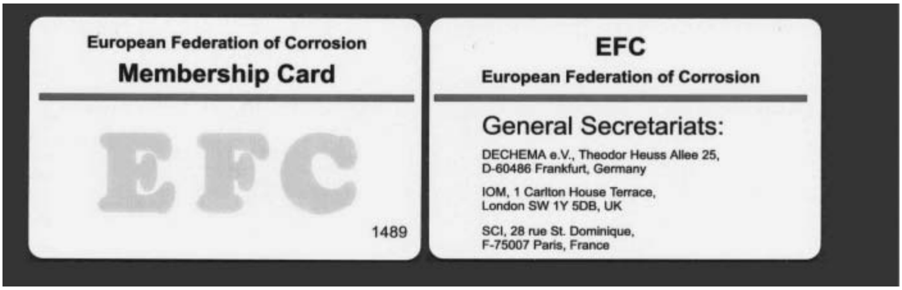
chairman. Since that date, three more EFC WPs have received final approved by the General Assembly: WP16 on Cathodic Protection, chaired by Marcel Roche (France) in 1999, WP17 on Automotive Corrosion, with Frits Blekkenhorst of The Netherlands as its first chairman, in 2000, and WP18 on Tribo-Corrosion, with Professor Jean-Pierre Celis of Belgium as its chairman, in 2002. At about the same time, WP12 on Computer Information Systems disappeared. This happened because WP12 differed from the other WPs in the way that it operated, much of its interaction taking place by electronic means. However, its former chairman, Professor Walter Bogaerts (Belgium), became instead chairman of EFC TF1 on Computer Applications, which is now associated with WP7 on Corrosion Education, chaired by Dr R. Cottis (UK).

In 2000, proposals from the Frankfurt office relating to the introduction of EFC membership cards for use by the members of EFC member societies were introduced.

1.15 Professor M. Schütze: EFC president 2006–2008

These cards (Fig. 1.16) entitle the bearer to discounted member's rates on other societies' products and events. For example, anyone belonging to an EFC member society participating in the scheme (and most now do) is entitled to a 20% reduction in the cost of the EFC books or up to €60 off the registration fee for EUROCORR 2005.

In 2001, Professor Kazimierz Darowicki (Poland) attempted to reactivate EFC WP2 on Corrosion and Protection of Structural Steelwork, following 16 years of inactivity. His attempts failed, largely because of concerns within the STAC that this would be impossible without duplicating activity within some of the other, more recently formed, WPs, such as WP14 on Coatings and WP16 on Cathodic Protection. Instead, in 2003, Professor Darowicki was appointed as chairman of a new EFC TF, TF2 on Focussed Applications in Corrosion and Protection of Steel Structures. The intention was that this would work between the existing WPs to tackle ad hoc problems requiring a multidisciplinary approach, drawing from the membership of those WPs as necessary. In fact, it has focused on the organisation of several workshops within Poland and nearby countries on topics as diverse as industrial heat exchanger problems, environmental degradation of structures, and the role of interfaces in corrosion and its prevention. This has done much to publicise EFC



European Federation of Corrosion

Membership Card

EFC

1489

EFC

European Federation of Corrosion

General Secretariats:

DECHEMA e.V., Theodor Heuss Allee 25,
D-60486 Frankfurt, Germany

IOM, 1 Carlton House Terrace,
London SW 1Y 5DB, UK

SCI, 28 rue St. Dominique,
F-75007 Paris, France

1.16 An EFC membership card

activity in the Baltic region and to encourage the formation of new corrosion societies in the Baltic states.

1.4 Cooperation with NACE International

In March 2003, on the occasion of the annual NACE Corrosion Conference in San Diego, Mr D. Harrop, president of the EFC, and Ms Elaine Bowman, president of NACE International (Fig. 1.17), signed an historic agreement on cooperation between the two organisations. This brought important benefits to both parties. In future, members of EFC member societies and those of NACE International will qualify for member rates when purchasing each others' products, including books, conference registrations, etc. Complimentary registrations to each others' annual conferences and stands at the associated exhibitions are also provided for the EFC and NACE presidents, and an accompanying person, under the agreement. As a consequence, both the EFC president and scientific secretary have so far been able to participate in NACEXPO events in Houston (2005), San Diego (2006), Nashville (2007) and New Orleans (2008).

1.5 EFC awards

For many years, the EFC has presented three awards in 2- or 3-yearly cycles. The European Corrosion Medal, the EFC's most prestigious award, consisting of a bronze medal, a diploma and the sum of €1000, has usually been presented every second year since it was instituted in 1985. The list of former laureates is included in Table 1.4. It is presented to a scientist or group of scientists for achievements in the application of corrosion science in the widest sense. On ten out of 11 occasions, the winner has been an individual (e.g. Fig. 1.18), but in 1999 it was presented to Professor G. C. Wood and his group at the Corrosion and Protection Centre in Manchester (Fig. 1.19).

1.17 Don Harrop (EFC) and Elaine Bowman (NACE) sign the NACE–EFC agreement, 19 March 2003

Table 1.4 Winners of the European Corrosion Medal (awarded for achievements by a scientist, or group of scientists, in the application of corrosion science in the widest sense)

1985	Dr A. Desestret	France
1987	Professor W. Schwenk	Germany
1989	Dr H. Arup	Denmark
1991	Dr. J Weber	Switzerland
1993	Professor A. Rahmel	Germany
1996	Professor R. N. Parkins	UK
1999	Professor G. C. Wood and colleagues	UK
2001	Professor E. Bardal	Norway
2003	Professor P.-L. Bonora	Italy
2005	Professor D. Landolt	Switzerland
2007	Professor E. Kálmán	Hungary

1.18 Professor P.-L. Bonora, winner of the European Corrosion Medal for 2003

The oldest EFC award is the Cavallaro Medal, a gold medal donated by the University of Ferrara as a memorial to Professor Cavallaro, the founder of its Aldo Daccò Study Institute and a member of the EFC's Scientific Advisory Council. Again, this is usually presented every other year, but this time to a scientist who is particularly distinguished by his activity and publications in the field of corrosion research. A list of the 20 winners since the award was instituted in 1965 is given in Table 1.5. These have included P. Gellings of The Netherlands (Fig. 1.20).

The third longstanding award is the Martí I. Franquès Award, comprising a silver medal and the sum of €500, to recognise individuals who have made outstanding contributions to the advancement of the science and technology of corrosion

1.19 Professor Graham Wood (left) receiving the European Corrosion Medal on behalf of himself and his colleagues at the UMIST Corrosion and Protection Centre from EFC president Philippe Berge in Aachen, 1999

Table 1.5 Winners of the Cavallaro Medal (awarded to a scientist who is particularly distinguished by his activity and his publications in the field of corrosion research)

1965	G. Bianchi (Italy)
1967	H. Fischer (Germany)
1969	P. Lacombe (France)
1971	U. R. Evans (UK)
1973	C. Wagner (Germany)
1975	M. Pourbaix (Belgium)
1977	T. P. Hoar (UK)
1979	E. Mattsson (Sweden)
1981	H. J. Engell (Germany)
1983	G. Trabanelli (Italy)
1985	R. N. Parkins (UK)
1987	G. C. Wood (UK)
1989	J. Oudar (France)
1991	P. Gellings (The Netherlands)
1993	J. E. O. Mayne (UK)
1995	F. Mazza (Italy)
1998	S. Smialowska (Poland)
2000	D. Landolt (Switzerland)
2002	A. Turnbull (UK)
2004	H. Gräfen (Germany)
2006	G. Thompson (UK)

1.20 Professor F. Zucchi (left) presenting the Cavallaro Medal to Professor P. Gellings (The Netherlands) in Budapest, 1991

through international cooperation within the EFC, transfer of knowledge, and education. Provided by the Spanish member society, SEQUI, between 1993 and 2003, and presented to the worthy winners listed in Table 1.6), this award was recently withdrawn. A replacement award is currently being sought by the Board of Administrators.

A fourth, more recent, award is the Kurt Schwabe Award. This was instituted by the Hungarian member society, HUNKOR, in 2000 in honour of the late Professor Kurt Schwabe. Consisting of a medal and the sum of €300, it is awarded every 3 years to a young scientist in recognition of his or her scientific and technical contribution to the field of corrosion on the basis of publications. As shown in Table 1.7, there have been three recipients to date, the first of whom was Dr Ilona Felhosi of Hungary (Fig. 1.21).

Table 1.6 Winners of the Martí Í. Franqués Award (awarded to individuals who have made outstanding contributions to the advancement of the science and technology of corrosion through international cooperation within the EFC, transfer of knowledge and education)

1993	S. Feliu	Spain
1996	E. Heitz	Germany
1998	A. D. Mercer	UK
2000	C. Cabrillac	France
2003	K. A. Tiller	UK

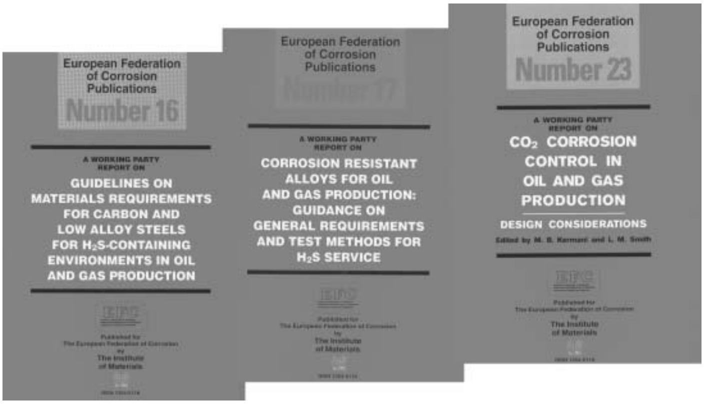
Table 1.7 Winners of the Kurt Schwabe Award (awarded to a young scientist in recognition of his or her scientific and technical contributions to the field of corrosion on the basis of publications)

2000	I. Felhosi	Hungary
2003	M. Ryan	UK
2006	T. Prosek	Hungary

1.21 Professor Erika Kálmán (left) presenting the Kurt Schwabe Award to Dr Ilona Felhosi (Hungary) in London, 2000

1.6 EFC publications

In 1989, the Institute of Metals, London, was appointed as the official publisher of the EFC series of publications that was then about to be launched. This arrangement still holds, but the books are now produced on behalf of the Institute of Materials, Minerals and Mining by Maney Publishing. Already, over 50 books in the distinctive green EFC livery have been produced (Fig. 1.22), and a number are currently in production. Full details are given in Table 1.8. Most of the books are still in print and may be ordered from Maney Publishing via its website (www.maney.co.uk). They are produced to the highest quality and are very well regarded by the corrosion fraternity.



European Federation
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Publications
Number 16

A WORKING PARTY
REPORT ON
GUIDELINES ON
MATERIALS REQUIREMENTS
FOR CARBON AND
LOW ALLOY STEELS
FOR H_2S-CONTAINING
ENVIRONMENTS IN OIL
AND GAS PRODUCTION

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of Corrosion
Publications
Number 17

A WORKING PARTY
REPORT ON
CORROSION RESISTANT
ALLOYS FOR OIL
AND GAS PRODUCTION:
GUIDANCE ON
GENERAL REQUIREMENTS
AND TEST METHODS FOR
H_2S SERVICE

European Federation
of Corrosion
Publications
Number 23

A WORKING PARTY
REPORT ON
CO_2 CORROSION
CONTROL IN
OIL AND GAS
PRODUCTION
DESIGN CONSIDERATIONS

1.22 Some of the best-selling EFC books, from EFC WP13

Table 1.8 The EFC Series

1	*Corrosion in the Nuclear Industry*	Prepared by the WP on Nuclear Corrosion
2	*Practical Corrosion Principles*	Prepared by the WP on Corrosion Education
3	*General Guidelines for Corrosion Testing of Materials for Marine Applications*	Prepared by the WP on Marine Corrosion
4	*Guidelines on Electrochemical Corrosion Measurements*	Prepared by the WP on Physico-chemical Methods of Corrosion Testing
5	*Illustrated Case Histories of Marine Corrosion*	Prepared by the WP on Marine Corrosion
6	*Corrosion Education Manual*	Prepared by the WP on Corrosion Education
7	*Corrosion Problems Related to Nuclear Waste Disposal*	Prepared by the WP on Nuclear Corrosion
8	*Microbial Corrosion*	Prepared by the WP on Microbial Corrosion
9	*Microbiological Degradation of Materials – and Methods of Protection*	Prepared by the WP on Microbial Corrosion
10	*Marine Corrosion of Stainless Steels: Chlorination and Microbial Effects*	Prepared by the WPs on Marine Corrosion and Microbial Corrosion
11	*Corrosion Inhibitors*	Prepared by the WP on Corrosion and Scale Inhibition
12	*Modifications of Passive Films*	Prepared by the WP on Surface Science and Mechanisms of Corrosion and Protection
13	*Predicting* CO_2 *Corrosion in the Oil and Gas Industry*	Prepared by the WP on Corrosion in Oil and Gas Production
14	*Guidelines for Methods of Testing and Research in High Temperature Corrosion*	Prepared by the WP on Corrosion by Hot Gases and Combustion Products
15	*Microbial Corrosion (Proceedings of the 3rd International EFC Workshop)*	Prepared by the WP on Microbial Corrosion
16	*Guidelines on Materials Requirements for Carbon and Low Alloy Steels for* H_2S*-Containing Environments in Oil and Gas Production*	Prepared by the WP on Corrosion in Oil and Gas Production
17	*Corrosion Resistant Alloys for Oil and Gas Production: Guidance on General Requirements and Test Methods for* H_2S *Service*	Prepared by the WP on Corrosion in Oil and Gas Production
18	*Stainless Steel in Concrete: State of the Art Report*	Prepared by the WP on Corrosion of Reinforcement in Concrete
19	*Sea Water Corrosion of Stainless Steels – Mechanisms and Experiences*	Prepared by the WPs on Marine Corrosion and Microbial Corrosion
20	*Organic and Inorganic Coatings for Corrosion Prevention – Research and Experiences*	Papers from EUROCORR ’96
21	*Corrosion–Deformation Interactions*	CDI ’96 in conjunction with EUROCORR ‘96
22	*Aspects of Microbially Induced Corrosion*	Papers from EUROCORR ’96 and the EFC WP on Microbial Corrosion

Table 1.8 Continued

23	*CO_2 Corrosion Control in Oil and Gas Production – Design Considerations*	Prepared by the WP on Corrosion in Oil and Gas Production
24	*Electrochemical Rehabilitation Methods for Reinforced Concrete Structures – A State of the Art Report*	Prepared by the WP on Corrosion of Reinforcement in Concrete
25	*Corrosion of Reinforcement in Concrete: Monitoring, Prevention and Rehabilitation*	Papers from EUROCORR '97
26	*Advances in Corrosion Control and Materials in Oil and Gas Production*	Papers from EUROCORR '97 and EUROCORR '98
27	*Cyclic Oxidation of High Temperature Materials*	Proceedings of an EFC Workshop, Frankfurt/Main, 1999
28	*Electrochemical Approach to Selected Corrosion and Corrosion Control Studies*	Papers from 50th ISE Meeting, Pavia, 1999
29	*Microbial Corrosion (Proceedings of the 4th International EFC Workshop)*	Prepared by the WP on Microbial Corrosion
30	*Survey of Literature on Crevice Corrosion (1979–1998): Mechanisms, Test Methods and Results, Practical Experience, Protective Measures and Monitoring*	Prepared by F. P. Ijsseling and the WP on Marine Corrosion
31	*Corrosion of Reinforcement in Concrete: Corrosion Mechanisms and Corrosion Protection*	Papers from EUROCORR '99 and the WP on Corrosion of Reinforcement in Concrete
32	*Guidelines for the Compilation of Corrosion Cost Data and for the Calculation of the Life Cycle Cost of Corrosion – A Working Party Report*	Prepared by the WP on Corrosion in Oil and Gas Production
33	*Marine Corrosion of Stainless Steels: Testing, Selection, Experience, Protection and Monitoring*	Edited by D. Féron on behalf of the WP on Marine Corrosion
34	*Lifetime Modelling of High Temperature Corrosion Processes*	Proceedings of an EFC workshop 2001, edited by M. Schütze, W. J. Quadakkers and J. R. Nicholls
35	*Corrosion Inhibitors for Steel in Concrete*	Prepared by B. Elsener with support from a task group of WP11 on Corrosion of Reinforcement in Concrete
36	*Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems*	Edited by D. Féron and Digby D. Macdonald of the WP on Nuclear Corrosion
37	*Test Methods for Assessing the Susceptibility of Prestressing Steels to Hydrogen Induced Stress Corrosion Cracking*	Prepared by B. Isecke of the WP on Corrosion of Reinforcement in Concrete
38	*Corrosion of Reinforcement in Concrete: Mechanisms, Monitoring, Inhibitors and Rehabilitation Techniques*	Edited by M. Raupach, B. Elsener, R. Polder and J. Mietz on behalf of the WP on Corrosion of Reinforcement in Concrete
39	*The Use of Corrosion Inhibitors in Oil and Gas Production*	Edited by J. W. Palmer, W. Hedges and J. L. Dawson

Table 1.8 Continued

40	*Control of Corrosion in Cooling Waters*	Edited by. J. D. Harston and F. Ropital
41	*Metal Dusting, Carburisation and Nitridation*	Edited by H. Grabke and M. Schütze
42	*Corrosion in Refineries*	Edited by J. D. Harston and F. Ropital
43	*The Electrochemistry and Characteristics of Embeddable Reference Electrodes for Concrete*	Prepared by R. Myrdal on behalf of the WP on Corrosion of Reinforcement in Concrete
44	*The Use of Electrochemical Scanning Tunnelling Microscopy (EC-STM) for Corrosion Applications and the Acquisition of Atomically Resolved Images: Reference Material (Cu Single-crystal) and Procedural Guidelines*	Prepared by R. Lindström, V. Maurice, L. Klein and P. Marcus on behalf of the WP on Surface Science and Mechanisms of Corrosion and Protection
45	*Local Probe Techniques for Corrosion Research*	Edited by R. Oltra, V. Maurice, R. Akid and P. Marcus on behalf of the WPs on Surface Science and Mechanisms of Corrosion and Protection, and Physico-Chemical Methods of Corrosion Testing
46	*Amine Unit Corrosion Survey*	Edited by J. D. Harston and F. Ropital on behalf of the WP on Corrosion in the Refinery Industry
47	*Novel Approaches to the Improvement of High Temperature Corrosion Resistance*	Edited by M. Schütze and W. Quadakkers on behalf of the WP on Corrosion in Hot Gases and Combustion Products
48	*Corrosion of Metallic Heritage Artefacts: Investigation, Conservation and Prediction of Long Term Behaviour*	Edited by P. Dillman, G. Béranger, P. Piccardo and H. Matthiesen on behalf of the WP on Nuclear Corrosion
49	*Electrochemistry in Light Water Reactors: Reference Electrodes, Measurement, Corrosion and Tribocorrosion*	Edited by R.-W. Bosch, D. Féron and J.-P. Celis on behalf of the WPs on Nuclear Corrosion and Tribocorrosion
50	*Corrosion Behaviour and Protection of Copper and Aluminium Alloys in Seawater*	Edited by D. Féron on behalf of the WP on Marine Corrosion
51	*Corrosion Issues in Light Water Reactors: Stress Corrosion Cracking*	Edited by D. Féron and J.-M. Olive on behalf of the WP on Nuclear Corrosion
52	*Progress in Corrosion – The First 50 Years of the EFC*	Edited by P. McIntyre and J. Vogelsang on behalf of the EFC Science and Technology Advisory Committee
53	*Standardisation of Thermal Cycling Exposure Testing*	Edited by D. Féron and M. Malessa on behalf of the WP on Corrosion in Hot Gases and Combustion Products
54	*Innovative Pre-treatment Techniques to Prevent Corrosion of Metallic Surfaces*	Edited by L. Fedrizzi, H. Terryn and A. Simões on behalf of the WP on Coatings
55	*Corrosion Under Insulation (CUI) – Guideline Applicable to Carbon–Manganese, Low Alloy Steels and Austenitic Stainless Steels Operating Between –4°C and 175°C*	Edited by Stefan Winnik on behalf of the WPs on Corrosion in Oil and Gas Production and Corrosion in the Refinery Industry

1.7 The EFC website

To mark the new millennium, the EFC established its own website in 2000. This is maintained by the Frankfurt office of the EFC, and provides a growing amount of information about the EFC, including:

- the current EFC Newsletter in full colour
- information about forthcoming events
- details of the EFC publications
- hot links to the EUROCORR congress sites
- the objectives and structure of the EFC and its: member societies (32), WPs (17), Board of Administrators , Science and Technology Advisory Committee, and General Secretariat.

The site (Fig. 1.23) is now being populated with web pages devoted to each of the WPs. These will outline the scope and objectives of each WP and provide a summary of their activities and other essential information.

1.8 Technical achievements of the EFC

The principal activities of the EFC are accomplished through its many WPs, whose activities are overseen and reviewed by the STAC. The chairman of the STAC is elected for 3 years and may be re-appointed for a second term (Fig. 1.24). The WPs are devoted to particular subjects within the broad fields of corrosion and its prevention. As a minimum, each WP is expected to organise a strong session at every EUROCORR conference when called upon to do so, either on its own or jointly with one or more other WPs with complementary interests (e.g. marine corrosion and microbial corrosion). However, there is scope for them to undertake many other interesting activities within their own fields, including: participation in collaborative research and testing programmes that could, for example, be aimed at underpinning

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The European Federation of Corrosion is a voluntary association of non-profit-making scientific and technical societies and association.

The purpose of the Federation is to contribute to the general advancement of the science of corrosion and of the protection of materials by promoting cooperation in Europe between scientific and technical societies and associations devoted to these areas of activity and by collaborating with similar associations throughout the world.

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September 4 - 8 2005, Lisbon, Portugal

September 25 - 28 2006, Maastricht, The Netherlands

http://www.efcweb.org/

1.23 The home page of the EFC website, www.EFCWEB.org

1.24 Dr Jörg Vogelsang, STAC chairman 2002–2007

future standard test methods; the organisation of courses, workshops, seminars and conferences; and the preparation of state-of-the-art reports, guidelines and proceedings for publication in the EFC Series. Detailed contributions from most of the working parties are included in following chapters of this volume. This final part of the introductory overview provides brief summaries on each of the WPs, based largely on information gleaned from EFC Newsletters published over the past 30 years [5–25].

1.8.1 WP1: Inhibitors

Under the chairmanship of Giordano Trabanelli, this was the first WP to be formed by the EFC. In addition to the organisation of sessions on inhibition at the EFC's corrosion conferences, it is best known for the series of European Symposia of Corrosion Inhibitors, which have been held at the 'Aldo Daccó' Study Centre of Ferrara University at 5-yearly intervals since 1960 (e.g. Fig. 1.25).

These symposia provide an opportunity for workers in the field of corrosion inhibition from all over the world to meet on a regular basis to discuss and review advances in the application of inhibitors and in the understanding of the mechanism of their action. The proceedings are published and can be obtained from the University of Ferrara. The 10th Symposium in the series (10th SEIC) took place in Ferrara from 29 August to 2 September 2005. It encompassed nine topics, including 'Impacts of legislative constraints on research, development and application of functional additives in corrosion and scale inhibition'. An International Summer School on Corrosion Inhibition was held at EPFL, Lausanne, during 1983 by Dieter Landolt and other members of the WP. Another important contribution from WP1 has been the organisation of a series of 5-day Intensive Courses on Corrosion Inhibitors at DECHEMA in Frankfurt, with both lectures and practical sessions. These began in September 1986 (Fig. 1.26), and four more have taken place since then (in 1988, 1993, 1997 and 2001).

1.25 Professor Franco Mazza addressing the 8th European Symposium on Corrosion Inhibitors (8th SEIC) at Ferrara University in 1995

1.26 Delegates at the first 5-day intensive course on corrosion inhibitors in Frankfurt during 1986

In 1994, WP1 contributed a book entitled *Corrosion Inhibitors* as No. 11 in the EFC Series. In 1995, the name of WP1 was changed to Corrosion and Scale Inhibition to reflect growing industrial concerns, and at its meeting in Riva del Garda in September 2001, the resignation of Giordano Trabanelli as chairman was announced. The new chairman, Günter Schmitt, has pledged to continue the series of Intensive Courses on Corrosion Inhibitors.

1.8.2 WP2: Corrosion and Protection of Steel Structures

Before being wrapped up by its chairman, R. Scimar, after its last meeting in 1985, WP2 prepared guidelines on the surface preparation of steel prior to the application of coatings and on the on-site application of coatings on metallic surfaces. Other projects concerned the protection of steel–aluminium structures and a comparison of different European standards on spray metallisation. In 1984, it jointly organised with APAC (the Belgian Association for Anti-corrosion Coatings) a successful conference that attracted 190 delegates. This highlighted the fact that there is no miraculous product for the protection of metallic structures against corrosion and, hence, the need for a real awareness of corrosion.

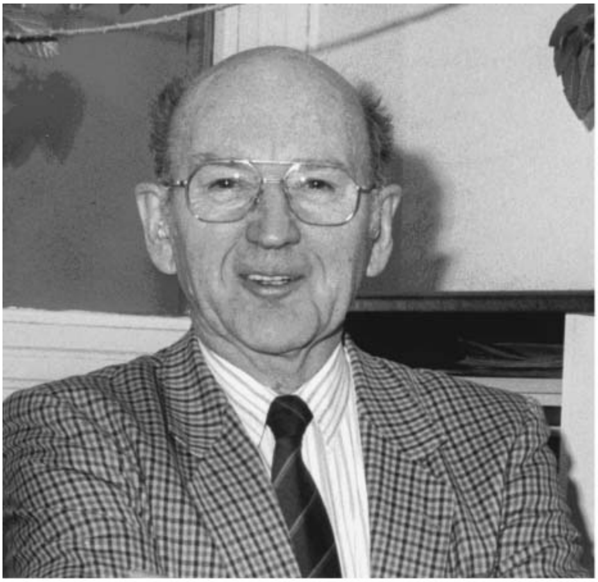
1.8.3 WP3: Corrosion by Hot Gases and Combustion Products

Under a succession of very active chairmen, including Alfred Rahmel (Fig. 1.27), Hans Grabke and, most recently, Michael Schütze, WP3 has contributed much to the aims of the EFC to promote cooperation within Europe to advance the science of corrosion and the protection of metals.

Under Michael Schütze's leadership, EU support was won for a proposal entitled COTEST – 'Cyclic Oxidation Testing', which involved 23 partners from the EU and associated states. The results from this programme will provide the technical basis for one of a series of new international standards being developed by ISO/TC 156/WG13 (High Temperature Corrosion) under the convenorship of Michael Schütze. WP3 has prepared six books for publication in the EFC Series (Nos. 14, 27, 24, 41, 47 and 53).

1.8.4 WP4: Nuclear Corrosion

Again, this WP has benefited from some extremely effective chairmen, all from France, including H. Coriou, Philippe Berge, François de Kéroulas, Jacques Daret and, now, Damien Féron. In recent years, it has organised and contributed to



1.27 Professor Alfred Rahmel, first chairman of WP3 international workshops and conferences in Bordeaux, Cadarache, Fontevraud and Nice. It has contributed six volumes to the EFC Series (Nos. 1, 7, 36, 48, 49 and 51). One of its key concerns at present relates to prediction of long-term corrosion behaviour in nuclear waste systems, which is the topic of two of its contributions to the EFC Series (Nos. 36 and 48). It is also concerned with corrosion issues for light water nuclear reactors, including corrosion predictions for lifetime extension, and corrosion issues for future nuclear systems. In its future programme, it will address irradiation-assisted stress corrosion cracking, the degradation of concrete, and microbial corrosion in nuclear waste systems.

1.8.5 WP5: Environment Sensitive Fracture

With the original title Stress Corrosion Test Methods, and under the chairmanship of Redvers Parkins in the 1970s, this WP published the first report to be published by an EFC WP, and in four languages, on a critical study of stress corrosion test methods. It then set about a collaborative testing programme to underwrite the series of ISO standards that appeared in the 1980s on a variety of stress corrosion cracking tests (ISO 7539, Parts 2–7). Although the round robin did not go entirely to plan, some useful results were obtained. In 1977 and 1978, the WP organised meetings in Newcastle and Firminy on slow strain rate stress corrosion tests and electrochemical test methods in stress corrosion testing. In 1985, the title of WP5 was changed to Environment Sensitive Fracture to broaden its scope. Thierry Magnin became chairman, and in 1992 organised a meeting on corrosion–deformation interactions in Fontainbleu. A 2-day meeting on stress corrosion cracking tests in St Etienne followed during 1995. A major event in 1996 was a second symposium on corrosion–deformation interactions, CDI'96, held in conjunction with EUROCORR '96 in Nice, the proceedings of which were published as No. 21 in the EFC Series. Later, WP5 participated in a collaborative European programme to compare the results from rising-load stress corrosion tests on pre-cracked specimens, which provided the basis for Part 9 of ISO 7539. Jean-Marc Olive succeeded as chairman in 2002, and organised the 2nd International Conference on Environmental Degradation of Engineering Materials (EDEM 2003) in Bordeaux in the following year, and a workshop on 'Stress corrosion and corrosion fatigue fractography'. In 2007, it contributed to No. 51 in the EFC Series, *Stress Corrosion Cracking in Light Water Reactors*, and Dr Krzysztof Wolski has since become its new chairman.

1.8.6 WP6: Surface Science and Mechanisms of Corrosion and Protection

WP6 was originally known as Surface Condition Influence on Corrosion, and had J. Talbot as its first chairman. In 1980, it changed its title to the present one and, under the chairmanship of Professor J. Oudar, during the mid-1980s organised a round robin exercise on the combined electrochemical and ESCA/AES characterisation of the passive film on Fe–Cr and Fe–Cr–Mo alloys, involving seven laboratories from France, Germany, Sweden, Switzerland and the UK. The results were presented at a workshop in Paris during 1986. In 1990, Philippe Marcus (Fig. 1.28) took over the chairmanship of the WP and held the European Symposium on Modifications of Passive Films in Paris in 1993, the proceedings of which were published as No. 12 in the EFC Series.

1.28 Philippe Marcus, chairman of WP6 and EFC vice-president

In 1994, a new long-term collaborative project to develop reference materials for scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) was initiated. This came to fruition in 2004 with the preparation of a report entitled *Use of Electrochemical Scanning Tunnelling Microscopy (EC-STM) for Corrosion Applications and the Acquisition of Atomically Resolved Images: Reference Material (Copper Single-crystal) and Procedural Guidelines*, which has since been published as No. 44 in the EFC Series.

1.8.7 WP7: Corrosion Education

One of the most ambitious projects of this WP, under the chairmanship of G. Svendenius (Sweden), was the production of three EFC films on corrosion during the 1970s and 1980s, in collaboration with the European Corrosion Education Foundation (ECEF). The ECEF was originally formed by the EFC Film Committee in the mid-1970s as a registered charity to collect the money needed to finance the production of educational films on important corrosion topics. The activity was pioneered by Professor J. S. L. Leach and his colleague at Nottingham University, Dr P. Boden. The sum of £17 000 was soon collected, and work on the first film, *Corrosion Control by Design*, began in 1976. This was completed within 2 years, and two further films, entitled *Corrosion Control by Coatings* and *Corrosion Prevention by Controlling the Environment*, followed over the next 10 years. When the ECEF was eventually wound up, the residual assets, including about £2500 in cash and the rights to the films, were transferred to the EFC.

The films have since been digitised, and are included in the distance learning materials that have been produced under the EU-supported MENTOR-C Project led by Walter Bogaerts, chairman of the EFC TF1 on Computer Applications, in which the EFC has been a partner. Publications from the WP have included EFC No. 2, *Practical Corrosion Principles*, and EFC No. 6, *Corrosion Education Manual*.

Stuart Leach succeeded G. Svendenius as chairman of WP7 in 1989 but, sadly, died only 2 years later. Between 1992 and 1996, WP7 was chaired by Professor D. Landolt,

1.29 Professor J. M. Costa, chairman of WP7 (1996–2004)

who was succeeded by J. M. Costa (Fig. 1.29). In recent years, it has established valuable web pages on the EFC website (www.EFCweb.org). Dr Robert Cottis (UK) succeeded Professor Costa as the chairman of WP7 in 2005.

1.8.8 WP8: Physico-Chemical Methods of Corrosion Testing

Originally called Physico-chemical Methods of Corrosion Testing – Fundamentals and Applications, WP8 developed under the chairmanship of Dr. L Clerbois and Mr R. Grauer, Belgium, with the aim of studying the bases and application of physico-chemical testing methods in the field of corrosion. It produced a report entitled *A Literature Review of Polarisation Resistance B Values for the Measurement of Corrosion Rate*, which was published by NACE. It also produced a paper, ‘Scaling of corrosion tests’, for the ISE meeting in Erlangen in September 1983, and went on to consider corrosion testing in non-aqueous media. A workshop on ‘Electrochemical corrosion testing with special consideration of practical applications’ was held at the Corrosion Study Centre ‘Aldo Daccó’ of the University of Ferrara in September 1985. This included techniques for the measurement of potential, current and polarisation. The proceedings were published as a monograph in the DECHEMA Monograph Series. In 1990, it produced a report, *Guidelines on Electrochemical Corrosion Measurements*, for publication as No. 4 in the EFC Series. It went on to organise a round robin exercise to compare the results obtained by several workers using different computer-assisted methods when studying the behaviour of one material in identical solutions. In 1994, Hans de Wit from The Netherlands (Fig. 1.30) became the new chairman of WP8.

The emphasis of the WP in recent years has been on the organisation of strong sessions at EUROCORR. Among the topics on which particular attention has been focused are good practice in electrochemical impedance measurements in corrosion science, and other techniques such as the Kelvin probe, the scanning vibrating electrode, and scanning reference electrode techniques.

1.30 Professor Hans de Wit, chairman of WP8 (1994–2006)

WP8 collaborated with WP6 to organise a workshop on ‘Local probe techniques for corrosion research’ during EUROCORR 2004 in Nice, and the proceedings have been published as No. 45 in the EFC Series.

In 2006, Dr Arjan Mol of The Netherlands succeeded Professor de Wit as chairman of WP8.

1.8.9 WP9: Marine Corrosion

The formation of this WP was proposed by the French member societies of the EFC following the International Congress of Marine Corrosion in Cannes from 8 to 15 June 1964. Its first chairmen included J. Talbot (France) D. B. Peplow (UK), and H. Arup (Denmark). Early activities included the preparation of a report on the stress corrosion cracking of welded high-strength steels in marine environments and a compilation of information on corrosion in heat exchangers in ships, power plants and offshore platforms. Two successful marine corrosion conferences were organised in Copenhagen, the second of which, in November 1984, dealt with corrosion problems in sea water cooling systems, including pumps, valves, piping and heat exchangers. WP9 went on to produce a report called *General Guidelines for Corrosion Testing of Materials for Marine Applications*, which was published as No. 3 in the EFC Series. By 1990, Professor F. P. IJsseling of The Netherlands was the chairman of WP9, and a collection, *Illustrated Case Histories of Marine Corrosion*, had been published as No. 5 in the EFC Series. In the following year, WP9 helped to organise an international symposium on marine and microbial corrosion in Stockholm. Another publication in the EFC Series, No. 10, *Marine Corrosion of Stainless Steels*, followed. In 1993, a major collaborative project was begun, to compare sea water corrosivity at 13 different European test stations. Bård Espelid, Norway, succeeded to the chairmanship in 1995, and further publications in the EFC Series followed, including: No. 19, *Sea Water Corrosion of Stainless Steels – Mechanisms and Experiences*; No. 30, *Survey of Literature on Crevice Corrosion (1979–1998)*; and No. 33, *Marine Corrosion of Stainless Steels; Testing, Selection, Experience, Protection and Monitoring*. For the past few years, WP9 has been heavily involved in the €650 000 EU-funded project 'Development of New Methods to Characterise the Durability of Stainless Steels to Crevice Corrosion in Natural and Treated Salt Waters' (acronym CREVCORR).

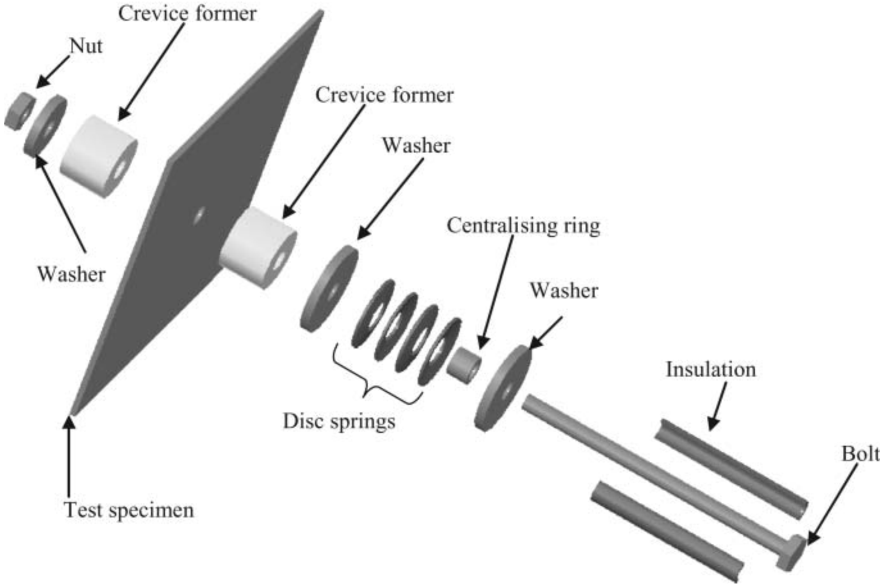
This has involved the development of a new formulation for synthetic sea water and collaborative testing to develop an improved electrochemical crevice corrosion test (Fig. 1.31).

This procedure has already been used successfully by the current chairman of WP9, Ulf Kivisäkk, Sweden (see below) [26], and it is intended to provide the basis for a new international standard test method via ISO/TC 156, WG11 (Corrosion of Metals and Alloys – Electrochemical Tests).

In 2007, the WP published its most recent contribution to the EFC Series, No. 50, *Corrosion Behaviour and Protection of Copper and Aluminium Alloys in Seawater*.

1.8.10 WP10: Microbial Corrosion

During 1987, plans were drawn up for the formation of two new EFC WPs, the first of which was WP10 on Microbial Corrosion. Mr A. K. Tiller (UK) was appointed as its first chairman, and the 1st EFC Workshop on Microbial Corrosion was held with support from Professor C. A. C. Sequeira and the local societies at Sintra in Portugal on 7–9 March 1988. This was followed by a second workshop at Sesimbra, Portugal, in 1991, the proceedings of which were published as No. 8 in the EFC Series. WP10 also arranged for an English translation of *Mikrobiologische Materialzerstorung und*



1.31 CREVCORR test method

Materialschutz (*Microbiological Degradation of Materials and Methods of Protection*) to appear as No. 10 in the EFC Series during 1992. Dominique Thierry, Sweden, then took over the chairmanship of WP10, and the 3rd Workshop on Microbial Corrosion was held in Estoril, Portugal, from 13 to 16 March 1994. The proceedings appeared subsequently as No. 15 in the EFC Series. Another book, No. 22, contained the proceedings of the session on microbial corrosion from EUROCORR 1996. The 4th Workshop on Microbial Corrosion took place in Lisbon on 6–9 June 1999, and the proceedings appeared as No. 29 in the EFC Series. At about the same time, WP10 began assembling a directory of European experts in microbially induced corrosion (MIC) and helped to establish a European network on MIC. In 2001, Rolf Gubner (Sweden) succeeded Dominique Thierry as chairman of WP10. Attention has been focused on the organisation of strong sessions at EUROCORR, including a workshop on 'Biofilms and materials in natural environments' at EUROCORR 2004, which included two keynote and 12 other oral presentations.

1.8.11 WP11: Corrosion in Concrete

Another of the new EFC WPs to be formed in 1987 was WP11 on Corrosion in Concrete, with Dr B. Isecke (Germany) as its first chairman. This quickly set about the preparation of reports on reference cells for use in concrete applications and on electrochemical rehabilitation techniques. In 1992, Professor C. L. Page (UK) took over as chairman of WP11, and new sub-groups were formed to study coated and corrosion-resistant rebars and design for durability. The WP's first publication, a state-of-the-art report called *Stainless Steel in Concrete*, appeared as No. 18 in the EFC Series in 1996. In the same year, Dr J. Mietz (Germany) became the new chairman of WP11, and the WP became involved in COST 521, a collaborative European programme on corrosion of steels in reinforced concrete structures, and RILEM WG154, on methods for the measurement of corrosion in concrete. In 1998, two further publications appeared, a state-of-the-art report called *Electrochemical Rehabilitation Methods for Reinforced Concrete* (EFC No. 24), and the proceedings of the session on 'Corrosion in concrete structures' from EUROCORR '97 (EFC No. 25). These were followed in 2000 by EFC No. 31, *Corrosion Mechanisms and Corrosion Protection*, in 2001 by EFC No. 35, *Corrosion Inhibitors for Steel in Concrete*, and in 2003 by EFC No. 37, *Test Methods for Assessing the Susceptibility of Prestressing Steels to Hydrogen Induced Stress Corrosion Cracking*. Two other reports, *Corrosion of Reinforcement in Concrete: Mechanisms, Monitoring, Inhibitors and Rehabilitation Techniques* (EFC No. 38), and *The Electrochemistry and Characteristics of Embeddable Reference Electrodes for Concrete* (EFC No. 43), have also been published recently, making WP11 the most prolific source of EFC publications, with eight in total. Michael Raupach (Germany) is the current chairman of the WP, which now has task groups on reference electrodes and corrosion models, and is participating in the COST 534 project on the protection of pre-stressed concrete.

1.8.12 WP12: Computer-based Information Systems

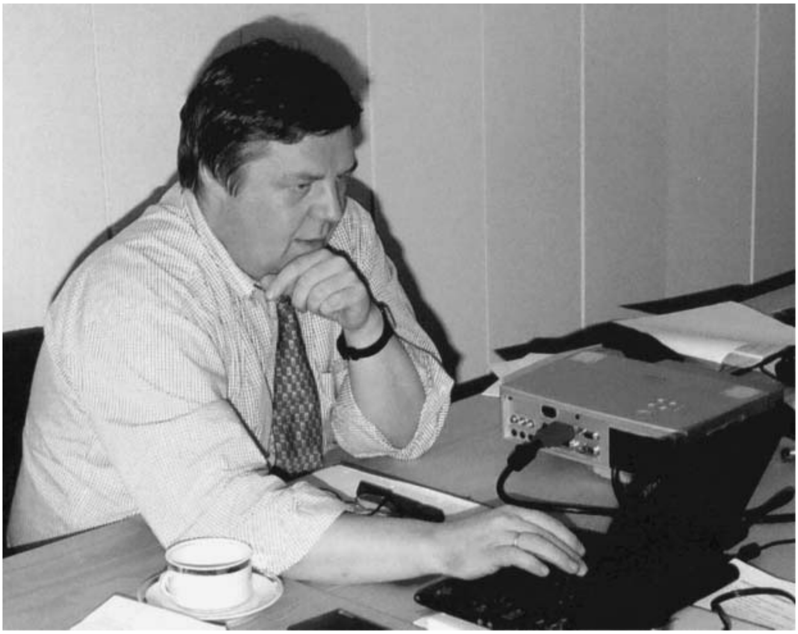
The formation of a new EFC WP on Computer-based Information Systems was approved by the EFC General Assembly in Brighton during 1988, and Dr R. Deplanque (Germany) was appointed as its first chairman. During its early years, the

WP was involved in establishing a successful MTI[†]/EFC/NACE WP on Expert Systems in Materials Engineering, with Dr Deplanque as chairman. In 1992, Dr Deplanque resigned. and his place as chairman of WP12 was taken by Professor W. Bogaerts (Belgium) (Fig. 1.32), whose aim was to promote awareness of European and worldwide activities in the area of computer-based corrosion and materials information systems and to establish a forum for dialogue between developers and active users.

The WP became involved in the BRITE-EuRAM thematic network action known as OCEAN (the Open Corrosion Expertise Access Network), the aim of which was to make existing corrosion information from databases, expert systems and multimedia systems more readily available by creating a European networked virtual community of corrosion expertise. In 2001, it was decided that because of their common interests, WP12 should merge with WP7 on Corrosion Education. Professor Bogaerts then took on responsibility for EFC TF1 on Computer Applications within WP7. This change coincided with the start of the EU-supported MENTOR-C Project, which has already been mentioned.

1.8.13 WP13: Corrosion in Oil and Gas Production

A proposal to form a new WP to address problems of corrosion in oil and gas production in a European context arose during 1991, and WP13 was quickly approved, with Dr L. M. Smith (UK) as its first chairman. Its inaugural meeting took place in Amsterdam during March 1992, and was attended by 39 members from ten different



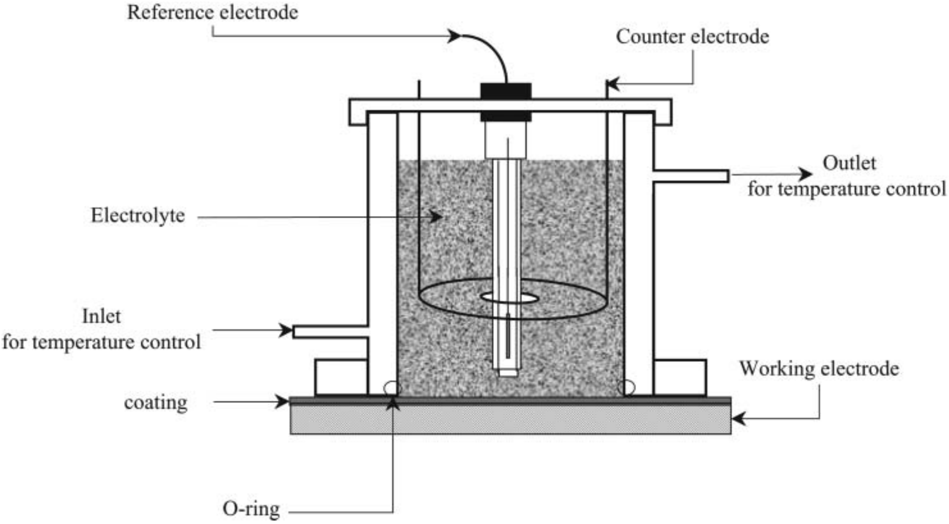
1.32 Professor Walter Bogaerts, chairman of EFC TF1

[†] Materials Technology Institute of the Chemical Process Industries (MTI), St. Louis, MO 63141

countries. Four working groups were established to deal with: sour service limitations of corrosion-resistant alloys; sulphide stress corrosion cracking of carbon and low-alloy steels; stepwise cracking of carbon and low-alloy steels; and MIC in oil and gas production. A fifth working group, on the inhibition of CO_2 corrosion, followed shortly afterwards, and the WP rapidly grew to become the largest in the EFC, with well over 200 members. Its first publication, EFC No. 13, *Prediction of CO_2 Corrosion in Oil and Gas Production*, appeared in 1994. However, a key issue for WP13 was materials for sour service and problems perceived with NACE MR0175, which, at the time, was the only recognised document on this topic. The WP's next two publications, EFC No. 16, *Guidelines on Materials Requirements for Carbon and Low Alloy Steels for H_2S Containing Environments in Oil and Gas Production*, and EFC No. 17, *Corrosion Resistant Alloys for Oil and Gas Production: Guidance on General Requirements and Test Methods for H_2S Service*, appeared in 1995 and 1996, respectively. These quickly established themselves as bestsellers among the EFC books and, having sold out, were both re-issued as second editions during 2002. They provided the technical basis for ENV 13797 2001, *Corrosion Protection – Carbon and Low Alloy Steels for Use in Hydrogen Sulphide Containing Environments in Oil and Gas Production – Materials and Test Methods – Guidelines*, and for ISO 15156 Parts 1–3. Another publication from WP13, EFC No. 23, *CO_2 Corrosion Control in Oil and Gas Production*, appeared in 1997. Mr P. S. Jackman (UK) succeeded Liane Smith as chairman of WP13 in 1998, and another book, EFC No. 26, *Advances in Corrosion Control and Materials in Oil and Gas Production*, appeared in the following year. In 2002, Mr Stein Olsen (Norway) took over the chairmanship of WP13. One year later, a WP report called *Life Cycle Costing of Corrosion in the Oil and Gas Industry* appeared as No. 32 in the EFC Series. The WP's most recent publication, *The Use of Corrosion Inhibitors in Oil and Gas Production*, appeared in 2004 as EFC No. 39. It has also been involved with WP15 in the preparation of EFC No. 55, *Corrosion Under Insulation (CUI) – Guideline Applicable to Carbon–Manganese, Low Alloy Steels and Austenitic Stainless Steels Operating Between –4^o and 175^{o}C.*

1.8.14 WP14: Coatings

During 1992, Professor P. L. Bonora (Italy) took steps towards establishing a new EFC WP on Coatings. This topic had originally fallen within the remit of WP2 on Corrosion and Protection of Steel Structures, which was, by then, moribund. Priority themes suggested for the new WP included environmentally friendly coatings and the evaluation of existing standards and specifications for coatings. In 1993, Professor Bonora was appointed as the first chairman of WP14, which organised its first full-day session at EUROCORR '94 in Bournemouth. Two years later, the selected proceedings of its session at EUROCORR '96 became No. 20 in the EFC Series. Professor Bonora's interests extended to the certification of coatings inspectors in Europe, and he organised two successful workshops on the topic, at EUROCORR '97 in Trondheim and at EUROCORR '98 in Utrecht. In 1999, an international workshop on the 'Application of electrochemical techniques to organic coatings' was held at Schliffkopf in Germany, and WP14 was also involved in the organisation of a session at ISE '99 in Pavia, Italy, the proceedings of which appeared subsequently as No. 28 in the EFC Series. In 1999, Dr J. Vogelsang succeeded to the chairmanship of WP14. As early as 1995, WP14 had turned its attention to the use of electrochemical impedance in the study of corrosion protection by organic coatings,



1.33 Example of cell used for EIS tests on samples with high impedance coatings (after [27])

and the new chairman soon formed a task group to develop a standard for electrochemical impedance spectroscopy (EIS), which met at Stuttgart in March 2000 and decided to undertake a collaborative test programme, using the apparatus shown schematically in Fig. 1.33.

This led subsequently to the establishment by Dr Vogelsang of a new working group of the International Organisation for Standardisation, ISO/TC 35/SC 9/WG 29, 'General test methods for paints and varnishes – Electrochemical methods', which met in Pittsburgh in June 2001 and agreed to develop a joint ISO/ASTM standard for the measurement of organic coatings by EIS. The first two parts of a multi-part international standard on EIS of high-impedance coated samples (ISO 16773) have now reached the Draft International Standard stage.

In 2001, Professor L. Fedrizzi (Italy) (Fig. 1.34) became the new chairman of WP14, which has since organised two international workshops on 'Electrochemical techniques applied to organic coatings', in Sintra, Portugal, in October 2003, and in Villars de Lans, France, in April 2005.

1.8.15 WP15: Corrosion in the Refinery Industry

This WP was approved by the EFC General Assembly in Nice during September 1996, with Dr J. D. Harston (UK) as its first chairman. It soon attracted over 50 members, keen to discuss topics of mutual interest, including: test methods for stress-oriented hydrogen-induced cracking (SOHIC); high-alloy materials for refinery use; corrosion in naphthenic acid-containing crude oils; materials for hydrofluoric acid alkylation units; bellows failures in refineries; and corrosion and cracking in amine plants. An early activity was a survey of problems in amine units, which remove acid gases such as H_2S and CO_2 by counter-flow against a lean amine gas. Data on over 20 amine units were collected. Another high-priority item, the treatment of cooling water systems, was identified in September 2000, and this led to the publication in 2007 of EFC No. 40, *Control of Corrosion in Cooling Waters*. In 2001,

1.34 Professor Lorenzo Fedrizzi, chairman of WP14 since 2001

Dr François Ropital (France) took over the chairmanship of WP15. Two new additions to the EFC series from WP14, EFC No. 42, *Corrosion in Refineries*, and EFC No. 46, *Amine Unit Corrosion Survey*, have been published recently. This WP provides an important forum for those working in the refinery industry, and its high level of activity is reflected in the fact that it organises two meetings per year.

1.8.16 WP16: Cathodic Protection

A proposal to create a new EFC WP on Cathodic Protection was made by Dr. Ph. Berge of CEFRACOR during the meeting of the EFC Board of Administrators in April 1998. This idea met with strong support, and WP16 held its inaugural meeting in Utrecht during September of that year, when Marcel Roche (Fig. 1.35) was appointed as its chairman.

The objective of WP16 is to develop the science and technology of cathodic protection for buried and immersed metal structures, including offshore structures, ships, pipes, and the internal parts of vessels. These aims are closely tied in with certification issues, including the certification of both personnel and cathodic protection companies. In 2000, it prepared a summary of the state of the art in this field, entitled *Qualification and Certification in the Field of Cathodic Protection: Present Situation and Possible European Scheme*, which compared the certification schemes in different countries. In 2002, WP16 was involved in a colloquium on ‘Corrosion certification: the European scheme’ and a seminar entitled ‘Cathodic protection and associated structures’, which took place back-to-back in Aix-en-Provence, France, from 4 to 7 June. Then, in response to an initiative from the EFC WP, CEN/TC 219 (Cathodic Protection) launched a new working group, WG5, on the Qualification and Certification of Cathodic Protection Personnel, with Marcel Roche as convenor, to prepare a European framework for the training, assessment and certification of cathodic protection personnel, defining levels of qualifications and fields of application. This

1.35 Marcel Roche, chairman of WP16

has already drafted a European Standard, EN 15257 'Cathodic protection – competence levels and certification of cathodic protection personnel', which was published during 2006. WP16 is planning to work with CEOCOR to produce a state-of-the-art report for the assessment of cathodic protection of buried pipelines, and helped to organise another cathodic protection workshop in Aix-en-Provence in June 2006.

1.8.17 WP17: Automotive Corrosion

Following the success of a special session on automotive corrosion at EUROCORR '98 in Utrecht, Professor J. H. W. de Wit (The Netherlands) proposed the formation of a new EFC WP on the topic, with the aim of guiding manufacturers, suppliers and material producers to make the optimum choice of materials combinations for durable, reliable and safe service. The inaugural meeting of WP17 took place during EUROCORR '99 in Aachen, and Mr F. Blekkenhorst (The Netherlands) was appointed as its chairman. Since then, WP17 has provided very well-planned sessions on automotive corrosion at each subsequent EUROCORR, and has provided an extremely valuable forum for discussion in an area where commercial considerations have often precluded open discussion between those working in the field. WP17 was also one of the first EFC WPs to establish its own web pages on the EFC website. Following the retirement of Frits Blekkenhorst, Dr Fouzia Hannour became the new chairman of WP17 in 2004.

1.8.18 WP18: Tribocorrosion

Tribocorrosion is a complex degradation process affecting metals and alloys that results from the combined effects of mechanical loading and environmental influences, and many aspects of the phenomenon remain to be elucidated. Against this background, a proposal to form a new EFC WP on Tribocorrosion was made by CEFRACOR, one of the two French EFC member societies, in 2002.

1.36 Professor Jean-Pierre Celis, chairman of WP18

The inaugural meeting took place in Granada during September 2002, and Professor J.-P. Celis (Belgium) (Fig. 1.36) was appointed as chairman. Seven TFs, each with distinct responsibilities and its own chairman, were formed: Science and Technology Watch; Inventory of Centres of Excellence; Inventory of Present and Future Industrial and Scientific Needs; Establishment of Specific R&D Actions; Standardisation; Knowledge Dissemination, Education and Training; and Sustainable Growth. Two round robin actions were launched in 2005, concerned with tribocorrosion of stainless steels and erosion–corrosion of stainless steels. These are partially funded by the EFC and supported by European industry, and will last for 3–5 years. WP18 helped to set up the 1st Summer School on Tribocorrosion Testing of Biomaterials in Lausanne from 8 to 9 June 2004. It also organised a 2-day workshop entitled ‘Tribocorrosion: industrial needs and scientific insights’ at EUROCORR 2004 in Nice, and the proceedings were published in *Wear* journal in 2006.

1.8.19 WP19: Corrosion of Polymer Materials

The EFC’s latest WP, WP19 on Corrosion of Polymer Materials, was officially approved by the EFC General Assembly at Lisbon in 2005. It was proposed during the previous year by GfKorr, one of the two EFC member societies in Germany, and received support from other societies in Austria, Belgium, France, Hungary, The Netherlands, Portugal, Spain, Sweden, Switzerland and the UK, well in excess of the minimum requirement of four-country support for the formation of a new EFC WP. Its inaugural meeting took place during EUROCORR in Nice on 16 September 2004, and Rudolf Morach (Switzerland) (Fig. 1.37) was appointed as its chairman.

Twenty-four people attended the meeting and it was followed by WP19’s first activity, a workshop on corrosion of polymer materials, which included seven most interesting presentations from leading experts in the field. It has to be admitted that the title of the new WP was the subject of much debate in the EFC STAC, chaired by Dr. J. Vogelsang. A vote about the acceptability of the title in the STAC ended in a

1.37 Dr Rudolf Morach, chairman of WP19

dead-heat, and it was decided to allow WP19 to choose its own name. The problem was that in the context of polymers, the term 'corrosion' defies the accepted ISO definition, which specifically refers to metals. However, WP19 has redefined corrosion as 'All processes involving the components of the material and medium which cause mass transport across the phase boundary and which may cause deterioration of the component or system.' The objectives of WP19 are 'To improve harmonisation of the theoretical understanding of corrosion mechanisms leading to the sustainable use and safe application of polymer materials, using a European network of experts to assemble the present understanding in the field of corrosion of polymers, identify the needs for further research, both in basics and application, evaluate existing testing methods, promote new investigation methods, and foster pre-normative work on an international basis.' Anyone wishing to participate in WP19 should, in the first instance, approach the EFC scientific secretary (paul.mcintyre@iom3.org).

1.9 The EFC today

1.9.1 Member societies

The introduction of membership subscriptions following the re-launch of the EFC as a registered non-profit organisation in 1984, and the merging or disappearance of some of the smaller societies, have resulted in a reduction in the number of EFC member societies from the high point of the mid-1970s, although there has been no reduction in the number of member countries represented in the EFC. As shown in Table 1.9, there are currently 32 member societies based in 25 different European countries, and the numbers are rising. An expression of interest in joining the EFC has been received recently from a society in Slovakia, and NACE Europe has applied for full membership, NACE International having been an associate member for 25 years.

Recently, the EFC has re-written its statutes to admit 'international members', i.e. corrosion societies located beyond the conventional boundaries of Europe, as defined

Table 1.9. EFC member societies (2007)

Country	Society
Albania	Albanian Corrosion Society, Professor Dr. Zana Gace, Bulevardi Zogu i 1-re 2, Tirana Tel: +355 42 490 81 E-mail: zgace@hotmail.com
Austria	Eisenhütte Österreich, Dr Heimo Jäger, c/o Montanuniverstät, Institut für Eisenhüttenkunde, A-8700 Leoben Tel: +43 384 245 189 Fax: +43 384 245 852 E-mail: asmet@unileoben.ac.at
Belgium	CEBELCOR, Ir. Antoine Pourbaix, Ave. des Petits-Champs 4A, B-1410 Waterloo Tel: +32 2 650 2791 gsm: +32 (0) 472 700 182 E-mail: apourbai@ulb.ac.be
Croatia	Croatian Society for Materials Protection, Dr. sc. Darko Rajhenbah, c/o University of Zagreb Fakultet strojarstva, ìbrodogradnje, Ivan Lucica 5, HR-10000 Zagreb Tel: +3851 6168 309 Fax: +3851 6168 343 E-mail: hdzama@fsb.hr
Czech Republic	AKI – Czech Association of Corrosion Engineers, Ing. Robert Bartoníček, CSc., Technická 5, CZ-16628 Praha 6 – Dijvice Tel: +42 224 31 0151 Fax: +42 224 31 1136 E-mail: aki@vscht.cz
	SVUOM Ltd, Professor Vladimir Cihal, Department of Corrosion Engineering, V Sareckem udoli 2329, 164 00 Praha 6 Tel: +420 235 355 851 Fax: +420 235 355 854 E-mail: kalabisova@svuom.cz
Denmark	Force Instituttet, Mr Peter Bo Mortenson, Park Allé 345, DK 2605 – Brøndby Tel: +45 4326 7000 Fax: +45 4326 7011 E-mail: force@force.dk
Finland	The Corrosion Society of Finland, Prof. Olof Forsén, Helsinki University, Laboratory of Corrosion, Vuorimìehentie 2, FIN-02150 Espoo Tel: +358 9451 2729 Fax: +358 9451 2798 E-mail: olof.forsen@tkk.fi
France	Centre Francais de l'Anticorrosion, CEFRACOR, Dr Gérard Pinard Legry, 28 rue Saint-Dominique, F-75007 Paris Tel: +33 1 4705 3926 Fax: +33 1 4555 9074 E-mail: cefracor@club-internet.fr

Table 1.9. Continued

Country	Society
	Société de Chimie Industrielle/Fédération Française pour les sciences de la Chimie, Mr Jean-Pierre Dal Pont, 28 rue Saint-Dominique, F-75007 Paris Tel: +33 1 5359 0213 Fax: +33 1 4555 4033 E-mail: sci.fr@wanadoo.fr
Germany	DECHEMA e.V., Professor Gerhard Kreysa, Theodor-Heuss-Allee 25, 60486 Frankfurt am Main Tel: +49 6975 64305 Fax: +49 6975 64201 E-mail: meier@dechema.de E-mail: honndorf@dechema.de
	Gesellschaft für Korrosionsschutz e.V. GfKORR, Dr.-Ing. Till Weber, Postfach 15 01 04, D-60061 Frankfurt Tel: +49 6975 64360 Fax: +49 6975 64391 E-mail: gfkorr@dechema.de
Hungary	Hungarian Corrosion Society ‘HUNKOR’, Dr Judit Telegdi, c/o Hungarian Academy of Sciences, Chemical Research Centre, Pusztaszeri ut 59/67, H-1025 Budapest Tel: +36 1325 7933 Fax: +36 1325 7509 E-mail: telegdi@cric.chemres.hu
Israel	Corrosion, Advanced Materials & Processes in Industry, CAMPI, Dr Amir Eliezer, Sami Shamoon College of Engineering, Corrosion Research Center, Bialik/Basel Sts., Beer-Sheva, Israel 84100 Tel: +972 86460127 Fax: +972 86460626 E-mail: campi@sce.ac.il
	Israel Corrosion Forum – NACE Israel, Dr Alec Groysman, Oil Refineries Ltd, P.O. Box 4, 31000 Haifa Tel: +972 4 878 8623 Fax: +972 4 8788371 E-mail: galec@orl.co.il
Italy	AIM – Associazione Italiana di Metallurgia, Professor Walter Nicodemi, Piazzale Rodolfo Morandi, 2, I-20121 Milano Tel: +39 0276 0205 51 Fax: +39 0276 0205 51 E-mail: aim@aimnet.it
	AITIVA, Associazione Italiana Technici Industrie Vernici e Affini, Professor Dino Mallamaci, Piazzale Morandi, 2, I-20121 Milano Tel: +39 0278 4969 Fax: +39 0278 4969 E-mail: info@aitivatriveneto.it
The Netherlands	Nederlands Corrosie Centrum – NCC, Mr Geert Reitsma, Postbus 190, NL-2700 AD Zoetermeer Tel: +31 79 353 1411 Fax: +31 79 353 1365 E-mail: ncc@fme.nl

Table 1.9. Continued

Country	Society
Norway	Norsk Korrosjonsteknìske Forening, Dr Torfinn Havn, c/o Aker Kvaerner, P.O. Box 589, N-4001 Stavanger Tel: +47 5189 8000 Fax: +47 5189 8263 E-mail: torfinn.havn@akerkvaerner.com
Poland	Polish Corrosion Society, Dr Agnieszka Krolikowska, c/o Road and Bridge Research Institute, Jagìellonska 80, PL-03301 Warsaw Tel: +48 22 811 9453 Fax: +48 22 811 3097 E-mail: akrolikowska@ibdim.edu.pl
Portugal	INETI, Instituto Nacional de Engenharia e Tecnologìa Industrial, Dr Elisabete Moreìra de Almeida, Estrada do Paço do Lumiar, 22, P-1649-038 Lisboa Tel: +351 21716 5141 Fax: +351 21716 0901 E-mail: elisabete.almeida@ineti.pt Sociedade Portuguesa de Materiais, Professor José Marat-Mendes, INETI – DMTP, Estrada do Paço do Lumiar, P – 1649-038 Lisbon Tel.: +351 21 716 51 81 Fax: +351 21 716 65 68 E-mail: jnm@fct.uni.pt E-mail: manuela.oliveira@ineti.pt
Romania	Corrosion Commission of the Romanian Academy, Professor Octavian Radovici, University Politehnica, Spl. Independentei 313, RO-069942 Bucharest Tel: +40 1 312 6879 E-mail: o.radovici@teh.prod.pub.ro
Russian Federation	ANTIKOR – International Scientific & Educational Corrosion Centre, Dr Alexandr V. Muradov, c/o Gubkin State University of Oil & Gas, Lenin Avenue, 65, 119991 Moscow Tel: +7 095 135 7286 Fax: +7 095 135 7286 E-mail: muradov@gubkin.ru
Serbia	Engineers Society of Corrosion, Professor Dr. Caslav Lacnjevac, Engineers Society of Corrosion, Kneza Milosa 9/I, 11000 Belgrade Tel: +381 11 2615 315 Fax: +381 11 193 659 E-mail: lcaja@agrifaculty.bg.ac.yu
Spain	Sociedad Espanola de Química Industrial, Dr Jaume Soley, Departamento de Ingenieria Química i Metalúrgia, Facultad de Química, Martí I Franquès 1, 6a Planta, E-08028 Barcelona Tel: +34 93 402 9013 Fax:+34 93 402 1291 E-mail: gonzalez@angel.qui.ub.es E-mail: jsoley@bflassociats.com
Sweden	Korrosionsinstitutet, Dr R. Gubner, Corrosion and Metal Research Institute (KIMAB), Drottning Kristinas väg 48, SE-114 28 Stockholm Tel: +46 867 41745 Fax: +46 867 41780 E-mail: rolf.gubner@kimab.com

Table 1.9. Continued

Country	Society
Switzerland	Swiss Society for Surface Technology, SGO, Dr Patrick Schmutz, EMPA Dübendorf, Überlandstraße 129, CH-8600 Dübendorf Tel: +41 1 823 4845 Fax: +41 1 823 4015 E-mail: Patrik.Schmutz@empa.ch
Turkey	The Corrosion Association, Professor Mustafa Doruk, Middle East Technical University, Metallurgical and Materials Engineering Department, 06531 Ankara Tel: +90 312 210 2516 Fax: +90 312 210 1267 E-mail: mdoruk@metu.edu.tr
Ukraine	Ukranian Association of Corrosionists, Professor Vasyl I. Pokhmurskii, Physico-Mechanical Institute, 5, Naukova Str. 290601 Lviv Tel: +380 322 63 1577 Fax: +380 322 63 1577 E-mail: pokhmurs@ipm.lviv.ua
UK	Institute of Corrosion, Mrs B. Peters, Corrosion House, Vimy Court, Leighton Buzzard, Bedfordshire LU7 1FG Tel: +44 1525 851 771 Fax: +44 1525 376 690 E-mail: admin@icorr.org The Institute of Materials, Minerals & Mining, Dr Bernard A. Rickinson, 1 Carlton House Terrace, London SW1Y 5AF Tel: +44 207 451 7367 Fax: +44 207 839 1702 E-mail: Bernie.Rickinson@iom3.org

by states that are full members of the Council of Europe. This means that all non-profit scientific and technical societies and organisations devoted to the advancement of the science of corrosion and of the protection of materials are now very welcome to become full members of the EFC. This change in policy has already resulted in the admission of two corrosion societies from Israel to the EFC fold. Other non-European societies may now approach EFC's Frankfurt secretariat for details of how to join the EFC (honndorf@dechema.de).

1.9.2 Membership of the Board of Administrators and STAC

Elections were held in the General Assembly in Freiburg during September 2007 for members of the EFC Board of Administrators and Science and Technology Advisory Committee to serve for 3 years from 1 January 2008 to 31 December 2010. The outcome is summarised in Tables 1.10 and 1.11, respectively, from which it is evident that the very desirable requirement of truly multinational representation on both bodies is being admirably met.

1.9.3 The EFC WPs

A full listing of the EFC WPs is given in Table 1.12. There are currently 17 active WPs and two TFs, each with its own chairman, as shown.

Table 1.10 Membership of the EFC Board of Administrators 2008–2010

Belgium	Mr Antoine Pourbaix (member country)
France	Dr Philippe Berge (founder member country)
Germany	Professor Bernd Isecke (founder member country)
UK	Mr Don Harrop (founder member country)
Croatia	Dr Sc. Darko Rajhenbah (elected)
Hungary	Professor Erika Kálmán (elected)
Italy	Dr Stefano Trasatti (elected)
Norway	Dr Stein Olsen (elected)
Russia	Dr Alexandr V. Muradov (elected)
Sweden	Dr Rolf Gubner (elected)

Table 1.11 Membership of the EFC Science and Technology Advisory Committee 2008–2010

France	Dr Damien Féron (chairman)
Albania	Mr Kastriot Betjaz (elected)
Germany	Dr Jörg Vogelsang (elected)
Hungary	Dr Judit Telegdi (elected)
Israel	Dr Amir Eliezer (elected)
UK	Mr Don Harrop (elected)
WP1	Professor Dr Günter Schmitt (Germany)
WP3	Professor Dr-Ing. Michael Schütze (Germany)
WP4	Dr Damien Féron (France)
WP5	Dr Krzysztof Wolski (France)
WP6	Dr Philippe Marcus (France)
WP7	Dr Robert Cottis (UK)
WP8	Dr Arjan Mol (The Netherlands)
WP9	Mr Ulf Kivisäkk (Sweden)
WP10	Dr Rolf Gubner (Sweden)
WP11	Professor Dr-Ing. Michael Raupach (Germany)
WP13	Mr Stein Olsen (Norway)
WP14	Professor Lorenzo Fedrizzi (Italy)
WP15	Dr François Ropital (France)
WP16	Mr Marcel Roche (France)
WP17	Dr Fouzia Hannour (The Netherlands)
WP18	Professor Jean-Pierre Celis (Belgium)
WP19	Dr Rudolf Morach (Switzerland)

At EUROCORR 2007 in Freiburg, the inaugural meeting of a new EFC WP on Corrosion and Corrosion Protection of Drinking Water Systems took place following a proposal from GfKORR. Dr Wilhelm Erning (Fig. 1.38) of the Federal Institute for Materials Research and Testing (BAM) in Berlin was elected as chairman of the new group, which, subject to the approval of the EFC General Assembly in Edinburgh in September 2008, will become WP20.

1.9.4 EFC events

Since the EFC was formed in 1955, a register of EFC events organised by its members, WPs and TFs has been maintained. EFC event numbers can be awarded

Table 1.12 The EFC working parties

Working Party title	Chairman
WP1: Corrosion and Scale Inhibition	Professor Dr Günter Schmitt, Germany (schmitt.g@fh-swf.de)
WP3: Corrosion by Hot Gases and Combustion Products	Professor Dr-Ing. Michael Schütze, Germany (schuetze@dechema.de)
WP4:Nuclear Corrosion	Dr Damien Féron, France (feron@ortolan.cea.fr)
WP5:Environment-snsitive Fracture	Dr Jean-Marc Olive, France (olive@lmp.u-bordeaux.fr)
WP6: Surface Science and Mechanisms of Corrosion and Protection	Dr Philippe Marcus, France (email: pmarcus@ext.jussieu.fr)
WP7: Corrosion Education	Dr Robert Cottis, UK (bob.cottis@manchester.ac.uk)
WP8: Physico-Chemical Methods of Testing	Dr Arjan Mol, The Netherlands (J.M.C.Mol@tudelft.nl)
WP9: Marine Corrosion	Mr Ulf Kivisäkk, Sweden (Ulf.kivisakk@sandvik.com)
WP10: Microbial Corrosion	Dr Rolf Gubner, Sweden (rolf.gubner@corr-institute.se)
WP11: Corrosion of Reinforcement in Concrete	Professor Dr-Ing. Michael Raupach, Germany (raupach@ibac.rwth-aachen.de)
WP13: Corrosion in Oil and Gas Production	Mr Stein Olsen, Norway (stol@statoilhydro.com)
WP14: Coatings	Professor Lorenzo Fedrizzi, Italy (Lorenzo.fedrizzi@uniud.it)
WP15: Corrosion in the Refinery Industry	Dr François Ropital, France (francois.ropital@ifp.fr)
WP16: Cathodic Protection	Mr Marcel Roche, France (marcel.roche@total.com)
WP17: Automotive Corrosion	Dr Fouzia Hannour, The Netherlands (fouzia.hannour@corusgroup.com)
WP18: Tribo-corrosion	Professor Jean-Pierre Celis, Belgium (jean-pierre.celis@mtm.kuleuven.ac.be)
WP19: Corrosion of Polymeric Materials	Dr Rudolf Morach, Switzerland (Rudolf.morach@cibasc.com)
TF1: Computer Applications	Professor Walter Bogaerts walter.bogaerts@mtm.kuleuven.ac.be
TF2: New Initiatives	Professor Kazimiertz Darowicki zak@chem.pg.gda.pl

to events satisfying the necessary criteria of quality and freedom from a direct clash with other pre-arranged EFC events. At the time of writing, 350 events have been registered as EFC events since 1955.

1.10 The future

In recent years, the EFC has continued to go from strength to strength, thanks to the continuing support of its member societies and, in particular, to the selfless

1.38 Dr Wilhelm Erning, chairman of the proposed WP20

contributions made by those who participate in its activities, usually with little or no support from EFC funds. Particular thanks are due to the chairmen of the WPs, who are true enthusiasts and give much of their time and effort to the good of the EFC. The officials of the EFC, including the president and vice-president and members of the Board of Administrators and the STAC, and the honorary treasurer, have also contributed enormously to the past development of the EFC, as have the hundreds of people who have participated in the work of its WPs, and those working at its three secretariats in London, Paris and Frankfurt.

Measures to improve the operation of the EFC are continuously under review, and one that will take effect from 2007 is the creation of a new EFC Congress Secretariat at the Frankfurt office. This will work with the local societies to improve further the quality of future EUROCORR events by providing a single point of contact for registrants and a more consistent approach to the organisation of both the conferences and their accompanying exhibitions. In this way, EUROCORR should be able to provide an increased financial return to the EFC, allowing the EFC to achieve even more in future.

Throughout its long history, the EFC has only had two paid members of staff, its scientific secretaries, working on a part-time basis at the rate of 1 day per week. Thus, it can be seen that the EFC punches well above its weight, having achieved an excellent international reputation for its activity while working on a rather modest budget. Provided that the level of support from its members and participants can be maintained in future, there is every reason to believe that it will still be going strong in another 50 years or more.

It is interesting to speculate on what will be the most important developments in the field of corrosion over the next 50 years. The increasing scarcity of chromium and other constituents of corrosion-resistant alloys is likely to make such materials prohibitively expensive in future. This is likely to focus attention firmly on the development of highly wear-resistant and corrosion-resistant coatings, particularly if self-healing properties can be achieved.

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2

Corrosion inhibitors in the mirror of five decades

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2.1 Introduction

Corrosion inhibitors are used today in a great variety of technical systems and processes, and represent an invaluable tool for highly efficient and cost-effective mitigation of materials corrosion. The progress in research and application of corrosion inhibitors was documented every 5 years at the famous European Symposia on Corrosion Inhibitors (SEICs), held in Ferrara, which from 1960 [5 years after the foundation of the European Federation of Corrosion (EFC) on 19 May 1955 in Frankfurt/Main] became a traditional, cultish event of EFC Working Party 1 on Corrosion Inhibitors. The organiser of the first Ferrara conference was the great Professor Léo Cavallaro, who was aleady among the plenary speakers on the first international conference organized by the EFC in Paris from 18 to 24 November 1956, i.e. 18 months after the foundation of the EFC. This contribution of Professor Cavallaro underlines the importance that was attributed by the international corrosion experts in the new EFC to corrosion inhibition as a special field of corrosion research and development. In memory of Professor Cavallaro, the first EFC medal was founded.

The 50th anniversary of the EFC therefore coincided with the 10th International Ferrara Conference on Corrosion Inhibitors. This adds justification to the present review of developments in the science and application of corrosion inhibitors during the last five decades in the mirror of the Ferrara conferences.

After highlighting the increase in knowledge of inhibitor performance in various media and technical applications, the paper will close with an outline on the needs for future development in corrosion inhibition, considering aspects and consequences of increasing environmental concern, emerging legal constraints and process-monitoring demands.

2.2 Mechanistic aspects

The mechanistic understanding of the action of additives influencing the reaction kinetics of metal dissolution and cathodic electron consumption in corrosion systems was improved significantly by the systematic considerations of H. Fischer and his co-workers [1,2]. For potential-dependent inhibitor action, Fischer differentiated between: (i) primary and secondary interface inhibition; and (ii) mechanical, chemical and electrochemical electrolyte film inhibition. In this scheme, primary inhibitors are adsorbed at the interface and remain chemically and electrochemically unchanged in the adsorbed state (inorganic species such as Cl^-, OH^-, or SH^-; organic species such as derivatives of the ammonium ion with N bonded to alkyl, cycloalkyl or aryl substituents or being a part of an aromatic and/or heteroaromatic system). On the other hand, secondary inhibitors are chemically and/or electrochemically converted in the adsorbed state (reduction of sulphoxides to sulphides [3], reduction of mercaptanes to disulphides [4], or decomposition of thio-compounds such as thiourea [5]).

Mechanical electrolyte film inhibition may be caused by colloids or suspensions, viscous solutions, or pores in polymolecular or polymerous layers; chemical electrolyte film inhibition may be the result of chemical reactions of substances with components of the homogeneous partial reactions of the electrode reaction, while electrochemical electrolyte film inhibition may be caused by changes of the ψ_1-potential in the diffuse part of the double layer, which are dependent on coverage of the interface with ions [2].

Much work was devoted to the first step of inhibitor action, adsorption. Many theoretical and experimental contributions to the effect of inhibitors on the electrode kinetics have been put forward during the Ferrara conferences. Only a few can be mentioned at this point, most of which consider adsorption phenomena at the plain, scale-free metal surface, as found, for example, on metal surfaces in contact with mineral acids. A general treatment was presented by R. Parsons in his plenary lecture of 1970 on adsorption phenomena influencing the kinetics of electrode reactions [6]. The principles of corrosion inhibition mechanisms dominated by adsorption phenomena were further outlined by G. Schmitt [7], considering blocking effects, dielectric effects and hydrophobic effects of inhibitor adsorption. It was shown in this paper that aggregation principles of compounds with amphipathic molecular structure encountered in the bulk liquid and at liquid–solid or liquid–gas interfaces can be used successfully to understand relative efficiencies of inhibitor additions, including structure–efficiency relationships. Thus, the long-known self-assembling properties of surface-active compounds, which ease the understanding of detergent (tenside) effects, emulsification–demulsification effects or solid–solid separation processes using flotation technology, could also be applied to understand corrosion inhibition mechanisms. With the use of atomic force microscopy (AFM), the ‘self-assembling’ effect of amphipathic molecules was later rediscovered, to become a fashionable keyword for a ‘new’ research field.

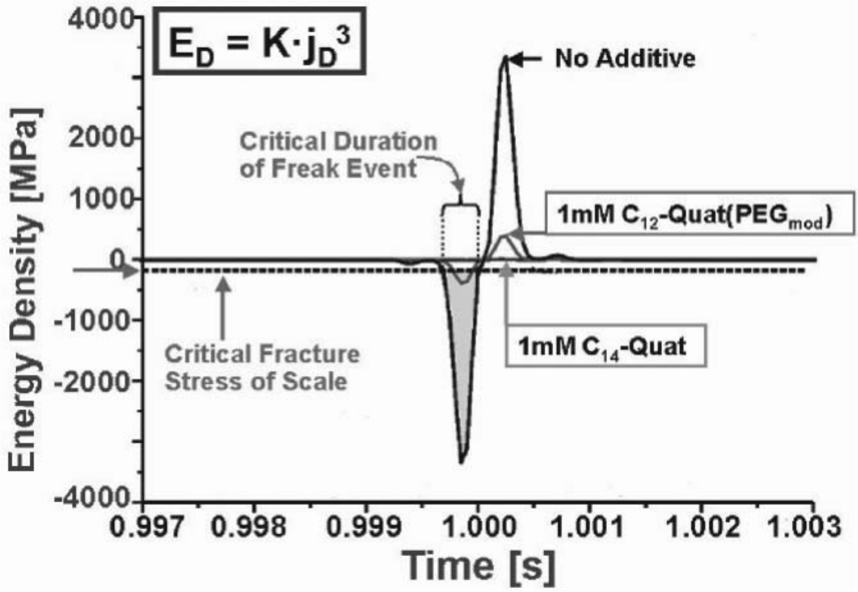
A theoretical approach to adsorption processes in acidic media was described by A. I. Krasilschikov [8], while K. Kobayashi and S. Fujii based their adsorption mechanism of organic corrosion inhibitors on steel in HCl solution on experimental results [9]. In the search for more general adsorption mechanisms, much work has been devoted to relationships between the chemical structure and inhibition efficiency of adsorbed species. One approach relates the efficiency to adsorption energies, using Temkin and Frumkin adsorption conditions [10], whereas others use charge distributions in the adsorbing molecule characterised, for example, in aromatic compounds via Hammett polar constants and Taft induction constants [11,12], or by molecular orbital calculations (the HOMO-LUMO approach) [13–16]. These approaches give satisfying structure–efficiency relationships generally only within one generic type of organic compound. Attempts have also been made to use Pearson’s Hard and Soft Acids and Bases (HSAB) principle [17,18] to explain inhibitor efficiencies [19], e.g. the adsorption behaviour of polar organic compounds [20–22].

More general applicability is exhibited by an approach of W. Durnie [23,24], who uses three to four intrinsic molecule properties (molar volume, dipole moment, HOMO-LUMO energy difference, and charge distribution in the molecule) to calculate the adsorption energy of compounds belonging to completely different generic classes of inhibitors, not only for scale-free but also for scale-covered metal surfaces. His approach is based on Temkin adsorption, and gives satisfying results for given degrees of coverage. Adjustment of the interaction factor would further improve the agreement between calculated values and experimental data.

However, with the exception of metal corrosion in mineral acids, almost all industrially important corrosion processes occur in the presence of corrosion product layers, some of which offer a significant degree of protection. Information on adsorption energies, therefore, has only a limited value, because corrosion inhibition in the presence of layers and scales follows a variety of mechanisms. R. H. Hausler showed [25] that corrosion inhibition must be understood in the light of the corrosion mechanism itself, since inhibition must either reduce the rate-determining process or create a new one. Therefore, Hausler differentiated between two-dimensional (2D) inhibition, where the inhibitor is adsorbed on scale-free surfaces (interface inhibition), and three-dimensional (3D) inhibition, where the inhibitor is incorporated in the scale covering a metal surface (interphase inhibition) [26]. This concept was later adapted by Lorenz and Mansfeld [27] to show the applicability of electrochemical impedance measurements for the investigation of 3D inhibition. With the development of scanning tunnelling microscopy (STM) and AFM, it became more than obvious that even those systems previously categorised as 2D systems are in reality 3D systems and have to be treated as such, because even the adsorption phenomena at the non-scaled interface (metal surface) can only be understood by considering the 3D character of the metal surface and the 3D properties of adsorbed molecules. What remains is the difference between the adsorptive interaction of adsorbates with surface metal atoms and the adsorptive interaction of adsorbates with surface metal compounds (i.e. corrosion product layers of oxides, sulphides, carbonates, phosphates, etc.).

However, at a time where corrosion science and, hence, corrosion inhibitor science was dominated by electrochemical approaches and techniques, it was important to improve awareness that electrochemical measurements, including AC impedance, are not necessarily in all cases the first choice for developing a better understanding of corrosion systems. Thus, Hausler showed [25] that the need to understand the corrosion mechanism stems from the fact that corrosion rate measurements, electrochemical or otherwise, must be related to the rate-determining step of the mechanism if the results are to have a predictive or diagnostic value. In the case of hydrogen sulphide corrosion of steel, inhibitors interfere with the electrochemical process occurring across the solid–scale interface. On the other hand, carbon dioxide corrosion of steel at elevated temperatures is inhibited through retardation of the dissolution of the iron carbonate scale layer. This latter effect cannot be observed by electrochemical means, e.g. in constant inventory autoclave tests. Such measurements, therefore, have no predictive value [25]. Later, it was demonstrated by G. Schmitt [28,29] that inhibitors affect the crystal growth rate of scales, producing thinner and less porous scales that exhibit higher resistance to cracking and spalling under high shear stress flow conditions [30,31]. This added the influence of corrosion inhibitors on the mechanical properties of protective scales to the spectrum of inhibitor effects to be considered in investigations on corrosion inhibitor mechanisms.

Another mechanistic aspect relating to the effect of corrosion inhibitors (and functional additives in general) on the resistance of metal surfaces to flow-induced



2.1 Effect of inhibitors on maximum energy densities of a flowing liquid with the wall under conditions of the "freak event"

localised corrosion has been intensely investigated [30]. It was found that some compounds exhibit drag-reducing properties when present at above a critical concentration (critical micelle concentration), which results in a reduction of the intensity of hydrodynamic interactions with the solid wall. With the 'freak event' concept, it was later possible [55] (Fig. 2.1) to quantify for the first time the maximum interaction intensity $I_{\max}$ or the maximum energy densities E_D from microelectrochemical current noise evaluation via wavelet transform of the noise data at a given time t_1 according to the equation:

$$I_{\max} = K\, j_D{}^3 = K\left[\sum_{\omega} \mathrm{A}(\omega)\sin\omega t\right]^3$$

The calibration factor K relates to the redox system used for measuring the diffusion-controlled current noise fluctuations. For the often applied hexacyanoferrate redox system, it was found [56] that:

$$K_{Red/Ox} = 3 \cdot \times 10^{-8} \quad Nm^4 A^{-3}$$

This allows calculation of the maximum energy density E_D for a freak event in current noise data from microelectrodes, which in the uninhibited case comes well into the range of fracture stresses of corrosion product scales and which can be reduced below the energy level needed to fracture and spall corrosion product scales (e.g. iron carbonates or iron sulphides) hydrodynamically.

It is assumed that micelle aggregates of amphipathic substances interact with near-wall turbulence elements at or in the viscous sub-layer of the hydrodynamic boundary layer and reduce the energy of micro-turbulences and, hence, the energy exchange with the solid wall.

2.3 Acid media

Papers in the first three or four Ferrara conferences (1960–1975) were dominated by basic investigations on the electrochemical nature of corrosion inhibition by adsorption. The majority of contributions dealt with iron and carbon steel in hydrochloric and sulphuric acids. Additives considered included N-, S-, P- and/or As-containing compounds, as well as acetylenic compounds. It was learnt that N-containing inhibitors (N bonded to alkyl, cycloalkyl or aryl substituents or being a part of an aromatic and/or heteroaromatic system) are more active in hydrochloric acid, while S-containing compounds [thiols (mercaptans), sulphides, sulphoxides, thioureas, other thio-compounds] are more efficient in sulphuric acid. Acetylenic compounds such as propargyl alcohol, 2-butyn-1,4-diol, or 1-octyn-3-ol proved their beneficial effects as additives to hydrochloric and sulphuric acid for application at elevated temperatures. However, in practical applications (pickling, surface cleaning, oil/gas well acidising), acetylenic compounds are generally not used alone, but in hydrochloric acid in combination with N-containing compounds, and in sulphuric acid in combination with S-containing compounds (e.g. dibenzyl sulphoxide) as well as with halide and/or pseudohalide ions, which need to be present to achieve good inhibition efficiency (synergistic effect). Structure–efficiency relationships were investigated in many publications, filtering out the most effective compounds within generic classes of inhibitors.

While most of the studies on inhibitor efficiencies were devoted to their influence on the anodic metal dissolution reaction, some work was also reported on the kinetics of hydrogen evolution and the inhibition and stimulation of hydrogen uptake in steel. One important study was made by M. Smialowski [32] on the inhibition and penetration of hydrogen in steels. The author showed that the presence in the electrolyte of inorganic and organic species containing hydrides of the elements B, P, S, As, Sb, Se, Te (or being produced in a cathodic reaction) enhances the penetration of hydrogen into metals such as iron, nickel, cobalt and steels. On the other hand, organic compounds that are adsorbed at the cathode as ions or molecules may inhibit the hydrogen uptake. The effect on the kinetics of hydrogen evolution was correlated further with the polar properties of substituents in aromatic N-containing inhibitors expressed in terms of Hammett constants [12]. It was also found that inhibitors producing HS^- ions upon decomposition (thioureas, salts of thioacids, thiocyanates, etc.) in the acid (probably also catalysed at the corroding metal surface) stimulate the hydrogen uptake of the metal [33]. A comprehensive work [34] showed that inhibitors of the metal dissolution rate would not necessarily inhibit the hydrogen uptake as well. This is especially true if H_2S is dissolved in the acid. Even commercially used acid inhibitors generally only inhibit the rate of metal dissolution, but fail to reduce the hydrogen uptake of the metal, specifically in the presence of H_2S. Therefore, the performance of acid inhibitors in reducing the metal dissolution rate and in inhibiting the uptake of cathodically produced hydrogen has to be evaluated in different experiments [35]. The hydrogen permeation method (hydrogen permeation rate indicated electrochemically or by measuring the time-related volume of permeating hydrogen) must be used in order to evaluate the inhibitor efficiency to prevent hydrogen penetration.

In order to differentiate between the different properties of acid inhibitors, W. Schwenk suggested in 1984 that additives that reduce the metal dissolution rate should be called ‘inhibitors’, while those that increase the metal dissolution rate should be named ‘stimulators’. On the other hand, additives increasing the rate of hydrogen penetration should be named ‘promoters’, while additives reducing the hydrogen uptake should be called ‘anti-promoters’ [38]. Good additives to inhibit the acid corrosion of metals should, therefore, exibit inhibitor as well as anti-promoter properties. The effect of additives to prevent metal uptake of hydrogen produced in the cathodic corrosion reaction has regularly attracted the attention of various research groups over the years, generally in connection with the question of hydrogen embrittlement of steel.

The preferred metal with which to study acid inhibition in hydrochloric and sulphuric acids was iron or mild steel. However, reports on inhibitors for stainless steels and non-ferrous metals were produced as well. Thus, potentiodynamic investigations were reported on the performance of primary amines, quinoline, dibenzyl sulphoxide and phenylthiourea in the inhibition of metal dissolution of stainless steel in hydrochloric acid [37]. Other publications focused on the effects of primary amines [38] or quinoline in combination with chloride on the (localised) corrosion of stainless steel (18-10 Cr–Ni) in sulphuric acid [39]. An electrochemical comparison of the performance of N-containing inhibitors (alkyl, cycloalkyl and aryl amines, pyridine) on corrosion inhibition of iron, copper and nickel in acids showed the great importance of the nature of the acid anion (HCl, H_2SO_4, $HClO_4$) and the type of metal on the degree of inhibitor efficiency [40]. With increasing numbers of Ferrara events, interest increased in studying the options for acid inhibition of non-ferrous metals and alloys. Amines and onium compounds were investigated as acid inhibitors for aluminium and its alloys, zinc, copper and brass. Copper and copper alloys could be protected in acids by sulphur compounds (thiourea, mercaptans, thiosemicarbazides), alkynols and N-containing compounds, e.g. benzotriazole (BTA). BTA, however, is more effective in neutral than in acid environments. The inhibition of zinc in acid media has been considered with phosphonium compounds as well as with Schiff bases.

Inhibitors for protecting titanium and zirconium in acid media (HCl, H_2SO_4) include multivalent ions (Fe^{3+}, Cu^{2+}, Ni^{2+}, Ce^{4+}), noble metal ions of the elements Ag, Pt, Au and Hg, oxidising mineral compounds (HNO_3, $K_2Cr_2O_7$, $KMnO_4$, KIO_3, Na_2MoO_4, $NaClO_3$, Cl_2, H_2O_2), oxidising organic compounds (nitro and nitroso compounds, azo compounds, quinone, anthraqinone and its derivatives) and complexing compounds (complexones). These inhibitors (except complexones) are effective only above critical concentrations; otherwise, increased corrosion attack is observed. Complexing organic compounds do not show such hazardous behaviour. The detrimental effect of fluoride can be best mitigated by complexing the fluoride ion [41].

A literature survey on pickling inhibitors covering not only acid corrosion of steel but also copper and stainless steel was presented at the 3rd Ferrara conference in 1970 by T. L. Rama Char [42]. Later surveys on acid corrosion inhibitors were performed by G. Schmitt within the activities of EFC WP1 on Corrosion Inhibitors, covering developments up to 1993 [43,44].

Inhibition in acid media has been a major subject in all Ferrara conferences. Very often, known systems were revisited when new investigation tools became available or new applications demanded information on extended ranges of parameters (e.g. temperature, flow). Studies were also triggered by new questions on the environmental impact of inhibitor compounds applied.

2.4 Neutral systems

Industrial systems that exhibit pH values near neutral (pH 5.5–9.0) and that need corrosion inhibitors to prevent corrosion failures predominantly include water-based heat transfer systems for cooling and heating. The selection of inhibitors depends on the type of cooling or heating system. Cooling systems can be: once-through systems; closed systems; or open systems.

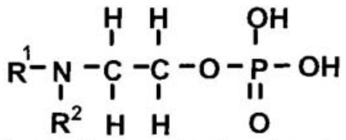
The classical once-through open system is the ship's condenser. Here, sea water freed from major organic bodies passes straight through the heat exchanger. Inhibition in the strict sense is not possible from the economic point of view. Therefore, the failure prevention strategy comes from the metal side: the use of corrosion-resistant materials (e.g. Cu–Ni alloys).

Closed systems include refrigerating brine, cooling liquids for engine cooling (glycol-based in the case of automotive engine coolants), and cooling liquids for solar heating systems. Although the systems are nominally closed, some possibilities for air ingress have to be considered (e.g. at the glands of pumps). In the selection of inhibitors, however, one has to consider not only the presence of oxygen but also dissimilar metal contact between cast iron, carbon steel, tin-coated copper, brass, aluminium alloys, and solder. Chromates at levels as high as 300–1000 p.p.m. have been used for a long time, together with considerable amounts of nitrite (up to 2000 p.p.m.). However, in mixed systems including the presence of copper and/or copper alloys among other metal materials, suppression of copper corrosion is the most important aim of inhibition: first, to prevent copper deposition on steel, zinc or aluminium with subsequent pitting corrosion; and second, to prevent glycol oxidation to corrosive glycolic acid, a reaction that is very effectively catalysed by copper ions. Therefore, all inhibitor packages contain copper corrosion inhibitors such as mercaptobenthiazole, BTA or tolyltriazole. Further additives – specifically for glycol-based automotive engine coolants – include sodium nitrite, benzoate, phosphate and borate, the latter two additives being used as reserve alkalinity (buffering agents). Silicates were used for this purpose as well. However, the formation of slimy deposits produced after some time of coolant usage led to the exclusion of silicates from modern inhibitor packages for glycol-based engine coolant, despite their efficiency for aluminium and its alloys. Over the years, chromates completely disappeared from the list of industrially used corrosion inhibitors for neutral systems, due to severe environmental concerns and legal restrictions. However, their wide range of applicability (ferrous and non-ferrous alloys over a wide range of pH) obviously fascinated researchers all over the world, as numerous publications are available showing the advantages and versatility of this famous anodic inhibitor. Today, research on chromate-containing inhibitors is a waste of time and money, not only because most questions have been answered, but also because this chemical is outlawed for environmental reasons.

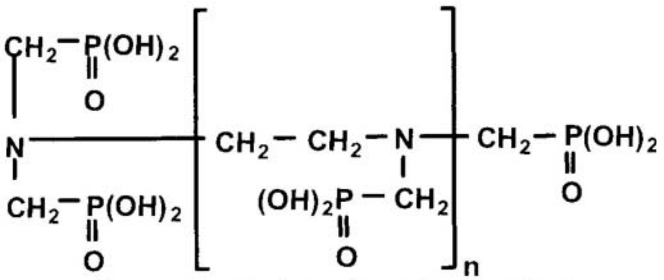
The decline of chromate usage can be followed over the years, specifically in open cooling systems with cooling towers. Driven by ecological considerations and environmental laws, treatment strategies for cooling water in open systems have seen significant changes in the types of industrially used treatment chemicals. Complications are caused by the fact that problems in open cooling systems arise not only due to corrosion, but also from scale deposition and biological fouling, both of which reduce efficiency of heat exchange and increase the likelihood of localised (under-deposit) corrosion. Thus, chemical treatment of open cooling systems needs corrosion inhibition as well as scale inhibition and biological control. While biological control in large cooling systems has long been achieved by dosage with chlorine or chlorine dioxide, the chemicals used for corrosion and scale inhibition have changed considerably over the years.

Although very efficient for inhibiting the corrosion of steel, sodium nitrite, frequently used in the mid-20th century, was soon substituted by polyphosphate (usually hexametaphosphate), because it was found that nitrite is readily degraded microbiologically, causing under-dosage of this anodic and therefore ‘dangerous’ inhibitor with subsequent localised attack. Polyphosphate, on the other hand, exhibits not only inhibitory but also scale-preventing properties, which can be significantly enhanced by the addition of small amounts of zinc ions. However, decomposition of polyphosphates to phosphate could stimulate calcium phosphate deposition in hard waters. Furthermore, phosphate has been blamed for the eutrophication (i.e. excessive growth of algae) of stagnant and slow-flowing surface waters and, therefore, the concentration of phosphate in the effluent from cooling systems is now controlled.

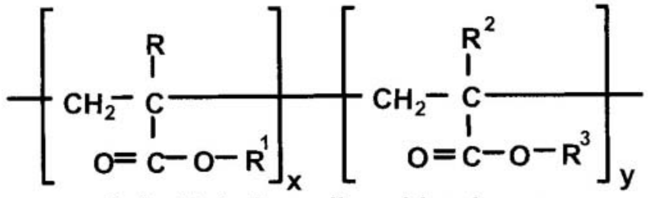
Sodium salts of phosphonic acids, such as 1-hydroxyethane-1,1-diphosphonic acid, aminomethylenephosphonic acid or diethyltriamine-pentamethylenephosphonic acid, and phosphonocarboxylic acids, such as phosphonobutane-1,2,4-tricarboxylic acid (PBTC) (Figs 2.2–2.4) became the basis of an all-organic concept of cooling water treatment, because such chemicals exhibit not only good corrosion-inhibiting efficiencies, but also dispersing activities, i.e. scale-preventing properties. Phosphonic



Typical phosphate structure
(di-substituted ethanolamine derivative)

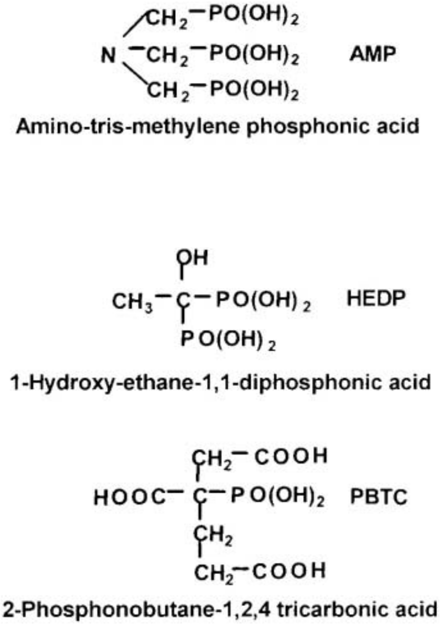


Generalized phosphonate structure

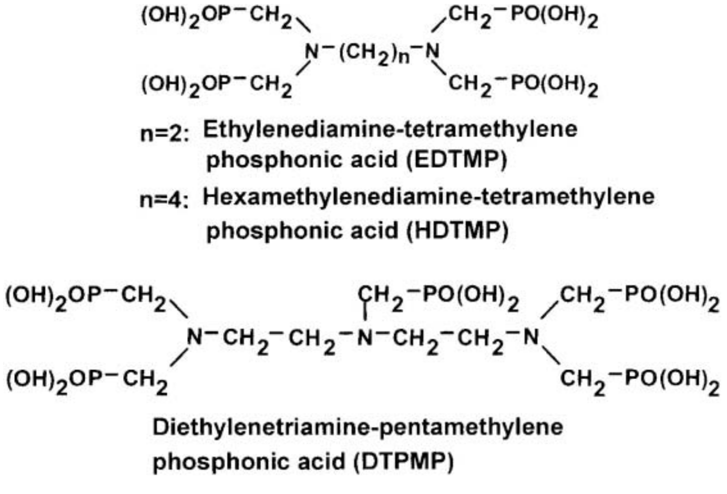


Substituted acrylic acid polymer

2.2 Generic structures of scale inhibitors



2.3 Structures of typical phosphonates



2.4 Structures of polyphosphonic acids

acid derivatives also show synergistic effects in combination with zinc ions and iron(III) ions, because such additions lead to a protective layer consisting of a three-dimensionally linked network of sparingly soluble iron and calcium phosphonate molecules. However, in the ‘all-organic concept’ currently followed in open cooling systems, inhibitor formulations used today are free of metal ions (Cr, Zn, Mo, V, etc.), nitrites and phosphates. Of the phosphonic acid derivatives, PBTC exhibits the best scale control properties with the lowest P content in the molecule and the highest resistance to degradation by Cl_2- or ClO_2-based biocides.

Table 2.1 Development of corrosion and scale inhibitors for cooling waters [47]

Need	Time frame	Types of inhibitors
Efficiency	Before 1960	Chromates, phosphates, nitrates, borates, silicate, Zn compounds
Economy	1960–1980	Cations, polyphosphates, gluconates, vanadates, molybdates, phosphono acids, polymers, carboxylates, surface active chelating agents
Ecology	1980–present	Tannins, natural compounds, surfactants, phosphono-organics, natural polymers, vitamins

Dispersants used additionally or as stand-alone treatments include polymers such as polymaleate, polymethacrylate, polyacrylic, polyacrylamide and polyaspartate.

Excellent reviews on inhibitors in neutral, specifically cooling water systems were given in Ferrara conferences by T. P. Hoar [45] and A. D. Mercer [46]. In 1994, E. Kálmán provided an excellent review up to 1992 on corrosion and scale inhibitors for cooling waters [47]. Specifically environmental concerns prompted long-known substances of low toxicity (e.g. tannins, gluconates) to be revisited and the performance of 'natural' products to be investigated. Table 2.1 illustrates the changes encountered in the last 50 years in the field of corrosion and scale inhibition in cooling waters [47].

Finally, in the last 15 years, developments have focused on 'green' inhibition and environmentally friendly inhibitors. This was mirrored also in the last two Ferrara conferences. An excellent review of green chemistry corrosion inhibitors for aqueous systems was presented by W. W. Frenier [48]. It appears that the first 140 pages of the first proceedings volume of the 9th Ferrara conference in 2000 were completely devoted to environmentally benign, environmentally friendly, low-toxicity and non-toxic inhibitors and scale-controlling agents for various fields of application [49]. Details should be taken from the cited literature.

2.5 Oil and gas industry

In the oil and gas industry, the application of inhibitors is an important and cost-effective technique to prevent corrosion failures. In production and pipeline transportation of oil and gas, corrosion problems arise from the presence of water and CO_2, H_2S, and in some cases, elemental sulphur. During acidification of hydrocarbon-bearing formations, corrosion of downhole equipment may occur due to attack by mineral acids (HCl or mixtures of HCl and HF) at elevated temperatures. In refineries, crude oil distillation units suffer corrosion attack by HCl, H_2S and naphthenic acids. Refineries can suffer corrosion by so-called gas waters, i.e. process waters from quench processes in fluid catalytic cracking or hydrocracking units. Corrosive ingredients include here mixtures of dissolved NH_3, CO_2, H_2S and HCN. In all such cases, corrosion inhibition is applied, in general very successfully.

Discussions and contributions on inhibitor efficiencies in the oil and gas industry were integral parts of Ferrara conferences from the outset. Important reviews include papers by J. I. Bregman in 1970 [50], Z. A. Foroulis in 1980 [51], and by both O. Lahodny-Sarc [52] and E. A. Bardasz [53] in 1985. The status of inhibitor development up to 1970 was excellently surveyed by J. I. Bregman [50] for inhibitor application in primary oil and gas production, secondary recovery (water flooding), pipelines, tankers, storage tanks and refinery streams or processes. The performance of inhibitors in downhole acidising was reviewed in 1970 by W. Machu and W. Dudlik [54].

Since the use of arsenic compounds was banned in the 1960s, due to their detrimental effect in poisoning reformer catalysts, the inhibitors used in producing wells have been exclusively organic in nature. They all have an amphipathic molecular structure in common; that is, they contain in the same molecule a hydrophilic (lipophobic, oleophobic, polar) and a hydrophobic (lipophilic, oleophilic, non-polar) moiety. The non-polar moiety generally consists of either unbranched hydrocarbon chains with 12–18 carbon atoms or, for example, polycyclic rosin derivatives, while the polar moiety predominantly contains one or more nitrogen atoms. Table 2.2 provides an overview of generic compounds and derivatives, together with typical molecular structures. This table is by no means comprehensive; however, it contains the 'workhorses' still used today in the petroleum industry. Although numerous papers have been published in the last 40 years (some at the Ferrara conferences) presenting new derivatives of known generic compounds and also some new chemical structures, the main development in corrosion inhibition in the petroleum industry has been triggered in the last 10–15 years by increasing concern about the environmental impact of industrially used functional chemicals.

2.5.1 Environmental aspects of chemical treatments

When chemicals are being selected for chemical treatments in the petroleum industry, environmental aspects have gained more and more importance. This is specifically true for offshore production, where a great proportion of the chemicals used is discharged into the water in one way or another. Statistics show that far more drilling chemicals are used and discharged than production chemicals. However, production chemicals may contain more toxic substances.

The predominant chemicals in produced water discharges are scale inhibitors, corrosion inhibitors and gas treatment chemicals, together representing about 80% of the total chemical discharge. Their environmental impact can be assessed from the discharge concentration with respect to the aquatic toxicity in terms of LC_{50} in p.p.m., measured for characteristic marine species (algae, crustacea and fish) (Table 2.3).

Discharged gas treatment chemicals include methanol and various glycols, all being water-soluble and easily biodegradable. The discharge concentrations are far below the LC_{50} values, and are not assumed to have any negative environmental impact.

Scale inhibitors are water-soluble and exhibit LC_{50} values above 1000 p.p.m. Average discharge concentrations are estimated to be in the order of 30 p.p.m. Acute toxicity is therefore not assumed to be a major concern. Scale inhibitors are mainly polyacrylates and phosphonates. The biodegradability of some of these products is low, and bioaccumulation may be possible.

The corrosion inhibitors and the biocides are the most toxic of the discharged treatment chemicals. They exhibit aquatic toxicities in the order of only 1–10 p.p.m. This indicates that discharges of corrosion inhibitors may have potentially negative effects on the marine environment.

Table 2.2 Inhibitors used in the petroleum industry

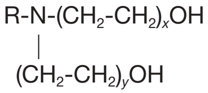
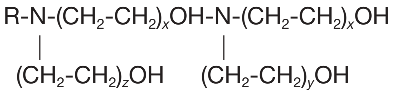
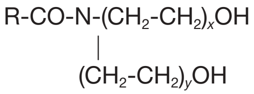
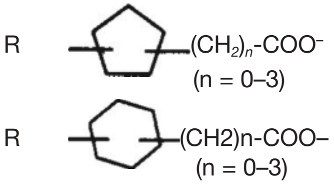
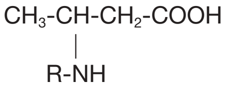
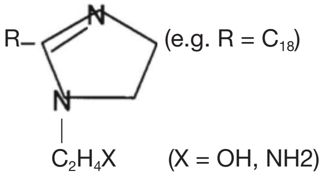
Main structure	Typical derivatives	Examples
Aliphatic fatty acid derivatives	Primary, secondary and tertiary monoamines	RNH_2; R_2NH, $R\text{-}N(CH_3)_2$
	Diamines	$R\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$
	Amides	$R\text{-}CONH_2$
	Polyethoxylated compounds: Amines	 $R\text{-}\underset{\substack{\vert\\(CH_2\text{-}CH_2)_yOH}}{N}\text{-}(CH_2\text{-}CH_2)_xOH$ ($x + y$ = 2–50)
	Diamines	 $R\text{-}\underset{\substack{\vert\\(CH_2\text{-}CH_2)_zOH}}{N}\text{-}(CH_2\text{-}CH_2)_xOH\text{-}\underset{\substack{\vert\\(CH_2\text{-}CH_2)_yOH}}{N}\text{-}(CH_2\text{-}CH_2)_xOH$ ($x + y + z$ = 3–10)
	Amides	 $R\text{-}CO\text{-}\underset{\substack{\vert\\(CH_2\text{-}CH_2)_yOH}}{N}\text{-}(CH_2\text{-}CH_2)_xOH$ ($x + y$ = 5–50)
	Acetic salts	$CH_3\text{-}COO^-$, e.g. salts of N-tallow propylenediamine
	Oleic salts	$CH_3(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COO^-$ e.g. salts of propylenediamine
	Naphthenic salts	 e.g. salts of propylenediamine
	Phosphate acid salts	$O{=}P(O)^{3-}$ e.g. salts of N-tallow propylenediamine
	Amphoterics: Amino acids	 $CH_3\text{-}\underset{\substack{\vert\\R\text{-}NH}}{CH}\text{-}CH_2\text{-}COOH$
Imidazolines		 (e.g. R = C_{18}) (X = OH, NH2)
Quaternary ammonium compounds	Alkyl, cycloalkyl and aromatic derivatives, including N as part of the aromatic or cycloaliphatic systems	$[R^1R^2N(CH_3)_2]^+$
Rosin derivatives	Rosin acids, rosin amines	

Table 2.3 Aquatic toxicity of chemicals

Generic chemical type	Aquatic toxicity LC_{50} (p.p.m.)	Discharge concentration (p.p.m.)
Methanol	> 10 000	< LC_{50}
Glycols	> 5000	< LC_{50}
Scale inhibitors (phosphonates, polyacrylates)	> 1000	ca. 30
Corrosion inhibitors	1–10	Not measured
Biocides (glutaraldehyde)	1–10	Not measured

In addition to the individual effects of the chemicals used, all components in the discharges may impose synergistic effects on the marine environment. These are, however, difficult to predict and would have to be established by testing in a variety of combinations.

Concerns about north-east Atlantic pollution from land-based and offshore sources prompted the establishment of a control system for the use and the discharge of offshore chemicals. This control system was developed by the Oslo–Paris (OSPAR) commission, a European body with members from states bordering the North Sea and Baltic Sea. OSPAR developed a Harmonised Mandatory Control Scheme consisting of: (a) the Harmonised Offshore Chemical Notification Format (HOCNF); (b) test protocols; and (c) definition of test species. The HOCNF contains information on the applied functional chemicals (chemical structure and properties, type of application, discharge, and environmental properties).

Detailed lists of requirements have been developed since around 1990 which must be met to receive discharge permits for chemicals used offshore. After a pre-screening [Is the chemical contained in the PLONOR (Possess Little Or No Risk to the environment) List and/or in Annex 2 of the OSPAR strategy? Is it inorganic in nature?], several requirements have to be fulfilled, e.g. biodegradability $>20\%$ in 28 days, toxicity (LC_{50} or EC_{50}) >10 mg/L (mostly *Skeletomena costatum*), high molecular weight beyond likelihood of bioaccumulation, or $\log P_{OW} < 3$ ($\log P_{OW}$ is the logarithm of the partitioning factor between n-octanol and water), hazard quotient < 1, and risk quotient < 1.

These regulations, first established for the North Sea and Baltic Sea region, today have been adopted more or less in many other parts of the world for offshore oil and gas production. Naturally, this was at the same time a big challenge for the selection and development of environmentally friendly treatment chemicals. For 'normal' production conditions, acceptable solutions seem to be available today. Intensive developments in functional chemicals are, however, needed, e.g. for deep hot wells, which are increasingly being exploited these days and present huge problems in corrosion inhibition.

2.5.2 Challenges for research and development of functional chemicals

The demand for environmentally more friendly functional chemicals and the rigid lists of requirements with more or less legal character clearly stimulated research and development in this field. On the other hand, national and regional laws and regulations that have been issued and enforced in the last two decades on the commercial use and transport of chemicals have dampened research and development (R&D) enthusiasm considerably, as they impose severe financial hurdles for the application of new chemicals that have not yet been included in the list of 'old' chemicals. Before even 1 kg of a new treatment chemical can be commercially applied, about €300 000 have to be spent in Europe and US$200 000 in the USA to complete mandatory tests for carcinogens and environmental hazards. What is more, this is on top of the high cost of innovative and pioneering R&D work and is a big burden for the development of new functional chemicals, which are generally designed to be effective in small quantities, and are not produced in big tonnages. Inevitably, the time to achieve a return on investment will be increased. As there is pressure to reduce this time for the benefit of stockholders, decisions to take such financial risks are likely to be made more and more reluctantly and only by large multinational companies where bulk chemicals are involved. This reduces significantly the opportunity to make the long-term strategic developments needed to meet, for example, the challenges posed by deep hot wells.

Strategic developments include new chemicals that not only fulfil the requirements of high performance for the envisaged purpose, chemical and thermal stability, compatibility with other treatment chemicals, and environmental demands, but also can be easily monitored in their active concentration (preferably online and also at remote sites). Monitoring demands will become more and more important in future production from difficult-to-operate wells, such as deep hot wells. An interesting concept is the intended modification of appropriate chemicals with tracers that can be used for online monitoring, e.g. by spectroscopic means. The tracer would be a structural part of the functional compound and should, of course, not adversely affect the product requirements listed above. The tracer concept is unlikely to be achieved by short-term projects, so is not likely to be realised in the near future.

The same fate can be foreseen for projects aimed at the development of multifunctional chemicals which, for example, act not only as scale inhibitors but also as corrosion inhibitors, hydrate inhibitors and drag reducers, and can also be monitored easily. Such an 'egg-producing-wool-milk-pig' would be intriguing because, for example, the dosing and compatibility problem should be very much reduced. Where is the management that dares to take long-term R&D decisions on functional additives for future oil and gas production? Where are the public funding programmes that would enable academic research to focus on such subjects?

The consequence of all this is that, in future, the development and application of new products with new innovative chemical design will be the rare exception rather than the rule. However, what remains to be done in industry and academia with 'old' chemicals in order to meet the challenges for future functional additives in oil and gas production is still tremendous and can have great scientific appeal.

'Old' chemicals and those 'new' chemicals that have been approved for other purposes than oil and gas treatment can, for example, be revisited or tested for applicability under deep hot well conditions, i.e. for corrosion inhibition, scale inhibition, drag reduction, emulsification, demulsification, etc., at temperatures above 150 °C and pressures up to 200 MPa in the presence of high-salinity waters and high partial pressures of CO_2 and H_2S, and, possibly, elemental sulphur. The thermal and chemical stability of such chemicals is one question; others are related to the special properties of supercritical media encountered under these conditions. Thus, phase behaviour, hydrocarbon/brine partitioning, wetting properties of exposed metallic surfaces, influence on corrosion and inhibition mechanisms, scale or hydrate precipitation kinetics, flow behaviour, possibilities for drag reduction and other treatment-related issues are completely unknown for such media and conditions. This opens a huge new field of fundamental and applied research related to the industrial production of oil and gas.

Of course, such R&D has to use more sophisticated and therefore more expensive technologies and methodologies than those generally applied so far. High-temperature, high-pressure experimentation under highly corrosive conditions is needed to go beyond existing knowledge frontiers. Everything becomes more difficult under such conditions; however, this can be managed, and should challenge academic and industrial fundamental and applied research. The situation of R&D of functional chemicals in oil and gas production can be compared with the R&D situation in the production of polymers and plastics. Here, research is no longer focused on new monomers (as it was between 1930 and 1970), because all monomers with technical relevance have been identified already. The challenge is more in combinations (co-polymerisation), production technology, and blending of intermediate and final polymeric products to create new materials with tailor-made properties. Also, R&D in this field is very innovative, effective and successful. We now have the same situation in the field of functional additives in oil and gas production. We have to admit the need to use primarily known tools (i.e. 'old' chemicals) for the solution of new problems. Nevertheless, there is great potential to use 'old' chemicals intelligently and innovatively for new applications, stimulating both academic and industrial research and development.

2.6 Inhibitors in coatings

Organic coatings are designed to exhibit barrier properties to protect the base material from attack by the environment. However, in reality, organic coatings act more like a membrane, because they are permeable to gases (oxygen and water vapour) and even ions (via water-rich preferred paths in the coating). Therefore, attempts have long been made to add inhibitor-releasing additives or corrosion inhibitors that are able to migrate through the coating to the metal–coating interface and/or can be leached out if scratches occur to provide protection against corrosion attack.

Red lead has been found to be very effective in primer coatings, and was therefore used successfully for many decades. Environmental concerns resulted in a ban on red lead as a primer component, and chromate-based inhibitors were used instead. Typical inhibitors include zinc or strontium chromate. However, chromates also came into the environmental discussion, and many investigations in the last 15 years were devoted to chromate-free substitution products. It is interesting to note that in the Ferrara conferences, only one paper was devoted to inhibitors in coatings in 1965 [57], two papers in 1985, five or six papers in 1990, and two in 2000. Reports on inorganic candidates [58,59,61,62,64] dealt with titanium dioxide, zinc or strontium or cerium molybdate, sodium molybdate, zinc phosphate, barium metaborate, cerium sulphate, cerium formate, and strontium metavanadate. Organic candidates included tetraethylammonium metathiovanadate [64], zinc salts of mercaptocarboxylic acids (thioglycollate, thiolactate, mercaptopropionate, dimercaptosuccinate) [58,59,63], organic mercapto compounds (2-thiohydantoine, 2-mercaptobenzthiazole, 2-mercaptopyrimidine, 2-mercapto-4-methyl-pyrimidine, 2-mercapto-4,6-dimethyl-pyrimidine) [59], BTA [64], furfurylglycidin [60], N-containing epoxipolymer [60], tannins [65], and imidazolines [61]. Such additives were tested in primers for steel and aluminium alloys, specifically those used in the aerospace industry.

As a general result, it appears that none of the substitutes tested so far compares with the performance of chromate-based pigments. This was very clearly shown in a comprehensive paper [64] presented in 2000. Today, other approaches are being explored in an attempt to increase the protectiveness of primers and paints. One is the application of self-assembled molecules (amphipathic phosphonates, silicates, mercaptans, etc.) as the first (mono) layer on the metal surface, which is subsequently coated with a primer. However, this approach cannot offer the self-healing effects of chromate-based primer modifications.

2.7 Inhibitors in concrete

Inhibitors for rebar corrosion protection in concrete have been a topic at Ferrara conferences only since 1995. At this, the 8th conference, five papers addressed this subject. Its increasing importance was documented 5 years later by another eight papers. The background is that corrosion of reinforcing steel in concrete has become a major infrastructure problem around the world. Billions of dollars have to be spent annually for the repair of bridge decks and parking structures that have been damaged by de-icing salts. While corrosion inhibitors have been used in special circumstances for many years as admixtures for reinforced concrete, the increasing need for repair of corroded reinforced concrete structures brought the application of corrosion inhibitors in repair systems into the current discussion, specifically the application of inhibitors as a surface treatment for concrete structures suffering from rebar corrosion. This kind of seemingly simple and cost-effective application would avoid the need to remove carbonated and/or chloride-contaminated concrete from embedded steel bars.

While proprietary formulations were already applied in repair works to bridge decks and other structures, uncertainties over possible limitations of the efficiency of surface-applied corrosion inhibitors prompted numerous discussions and research activities from which a better general understanding of the applicability of corrosion inhibitors to reinforced concrete both as admixtures and as surface-applied remedial treatments has emerged.

2.7.1 Admixtures

Both inorganic and organic additives have been tested as inhibitive admixtures. The inorganic additives include nitrites, chromates, borates, phosphates, molybdates, tungstates, and divalent tin compounds, while the long list of organic additives includes alkanolamines, quarternary ammonium compounds, dicyclohexylamine and derivatives, benzoate derivatives, saturated dicarboxylate salts, polyhydroxylated compounds, acryl derivatives, and tannins of different origins. While many of these additives have been tested for efficiency only in synthetic 'pore electrolytes' or mortars [65–69], some have also been investigated in reinforced concrete [70,71].

Calcium nitrite is a commonly used inhibitor applied as an admixture. However, among other properties, calcium nitrite has the disadvantage of being an anodic inhibitor that is effective only above critical concentrations. Below such critical concentrations, it is likely to initiate localised attack. Furthermore, several European countries have banned the use of nitrites, for environmental reasons.

Suggested substitutes for calcium nitrite include the group of alkanolamines, specifically monoethanolamine, *N*-methyl-ethanolamine, *N*,*N*-diemethyl-ethanolamine, diethanolamine, and triethanolamine [71]. The mechanism of their efficiency is still under discussion.

Another interesting candidate is sodium monofluorphosphate. However, this compound, together with calcium nitrite and alkanolamines, has proved to be very sensitive to the chloride concentration [70]. Alkanolamines lose their efficiency when there is more than 0.6% chloride in the pore water.

2.7.2 Surface-applied remedial treatments

The application of inhibitors from the surface demands, in addition to efficiency in rebar corrosion inhibition, the ability to migrate through concrete. This is claimed to be the case for selected amine salts (e.g. dicyclohexylammonium nitrite or carbonate, and monoethanolammonium carbonate) in combination with surfactants. Commercial formulations are available based on this concept. Their penetrating ability has been shown in permeation and corrosion experiments [72–74]. However, their long-term efficiency is not yet clear.

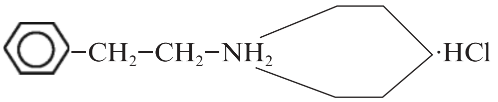
2.7.3 General remarks

The state of the art of corrosion inhibitors for steel corrosion in concrete has been recently summarised in EFC publication No. 35 [75], which describes in detail the different commercial inhibitors available for use in concrete, and considers their mechanistic action together with experience from laboratory and field tests. The report also deals with the possible effects of inhibitors on concrete properties and what is known of their long-term efficiency.

2.8 Vapour Phase Inhibitors (VCIs)

Vapour phase **C**orrosion **I**nhibitors or **V**olatile **C**orrosion **I**nhibitors are used for temporary corrosion protection - mostly for steel - during storage or transportation under otherwise corrosive conditions. VCIs are applied in wrapping papers, plastic films, sponge foams, waxes, oils and even aqueous solutions. The “workhorse” chemical, now used for more than fifty years, is DICHAN, i.e. dicyclohexylammonium nitrite, a white crystalline, odourless and relatively non-toxic compound. Its vapour pressure is 0.1 mbar at 21 °C and the solubility in water is 3.9 g/100 ml water. The pH of this saturated solution is 6.8. One gram of DICHAN will saturate 550 m^3 of air, rendering the air non-corrosive for steel and also for zinc. The efficiency on copper is less pronounced, but not zero.

Other VCI compounds include cyclohexylammonium carbonate, or, more generally, cyclohexylammonium carboxylates (CHAC). Cyclohexylammonium compounds are frequently used in combination with urea and sometimes also with sodium nitrate [76, 77]. In the early sixties chromates were still investigated in combination with tertiary alcohols (tert. butanol, tert. pentanol, or tert. hexanol) [78] or cyclohexylamine carboxylates obatined from higher molecular fatty acids (e.g. C_{16} - C_{18}) [79]. The aim was to achieve oil solubility and use the inhibited oil for temporary protection. Chromate-containing VCIs are no longer in use. Recent newly investigated VCI compounds include morpholine and its derivatives such as morpholine carbonate, borate, sorbate, laurate, succinate, azelate, sebacate and thiophenolate as well as hydrochlorides of aminopropiophenones [80], the most effective derivative of the last class of VCI being ß-piperidineaminomethylpropiophenone hydrochloride (PDPH) [80]:



(PDPH)

Furthermore, hydrazine-based compounds have been proposed as VCIs, e.g. reaction products of thiocarbohydrazides and organic acids. High efficiency was observed for steel with 1-benzylidine-3 -thiocarbohydrazide cinnamate (BTCHC) [81]:

(BTCHC) R = cinnamate

A more general theory-based approach to find new or more efficient VCI compounds was presented in 2000 by N. N. Andreev and Yu. I. Kuznetsov [82].

All of the most effective VCIs are reaction products of weak volatile bases with weak volatile acids. Such substances, although ionised in aqueous solutions, e.g. condensed water, undergo substantial hydrolysis, the extent of which is almost independent of concentration. In the case of ammonium nitrites and ammonium carboxylates the corresponding hydrolysis equations are:

$$(R_2NH_2)^+NO_2^- + H_2O \longrightarrow (R_2NH_2)^+ OH^- + HNO_2$$

$$(R_2NH_2)^+CO_2R^- + H_2O \longrightarrow (R_2NH_2)^+ OH^- + HOOC\text{-}R$$

VCI products are vaporised from the carrier solution in a pH range of 5.5 to 8.5. The inhibitor migrates to all recessed areas and cavities and condenses on metal surfaces. The inhibitor molecule is hydrolysed in moisture, and protective ions are attracted to the metal surfaces, forming a thin, protective, monomolecular film.

A great number of procedures are available for testing the performance of VCI-treated materials (papers, films, emitters, foams, powders, and oils). However, many of these tests are not very satisfactory with respect to the reproducibility of results. A comprehensive and critical overview was given in [83].

2.9 Development of investigation and testing tools

The increase in knowledge and understanding of mechanistic effects and efficiencies of corrosion inhibitors has been directly influenced by technical developments over the last 50 years. The development of easy-to-use, more or less inexpensive potentiostats at the beginning of the 1960s triggered a huge number of investigations on the electrochemical nature and mechanisms of corrosion inhibition. The number of inhibitory substances that have been introduced into potentiostatic and potentiodynamic measurements is enormous.

The general idea was to use such measurements as a quick tool to prove inhibitory efficiency by determining corrosion rates with the Stern–Geary method (polarisation resistance) or by the extrapolation of Tafel lines, and by establishing the anodic or cathodic nature of the inhibitory action. In the 1970s and 1980s, investigations with electrochemical impedance spectroscopy (EIS) dominated scientific efforts to increase the mechanistic understanding of corrosion inhibition. This method allows not only investigation of the rate-determining step in the corrosion reaction – as is the case with potentiostatic/dynamic or galvanostatic/dynamic measurements using potentiostats – but also basic analysis of all the steps in the corrosion reaction. The advanced development of computer technology at that time allowed a vast amount of data to be handled in both data acquisition and data evaluation. This made it possible to evaluate the relevant transfer functions from EIS measurements for modelling the relevant steps of the corrosion reactions by means of equivalent circuits. EIS proved its value as an experimental tool with which to improve the understanding of electrochemical processes. Time-related effects of inhibitor properties on double-layer capacitances and polarisation resistances could be easily evaluated, although not all researchers applying EIS extracted all of the information contained in the EIS data. Many investigators used to, and still do, use EIS only as a very expensive tool with which to identify time-related polarisation resistances.

With EIS, other transient methods came into fashion in electrochemical laboratories, such as cyclic voltammetry, pulse methods or electrochemical noise diagnostics. With time, the advances and drawbacks, i.e. the limits of application and levels of information of the different electrochemical methods, became appreciated and were brought to the attention of potential users. Recent years have seen a great movement towards electrochemical noise (ECN) measurements, which contain, among other features, the unique option for online identification and monitoring of localised corrosion. The author of this paper forecasts that with optimised data acquisition and improved user-friendliness in data evaluation, ECN diagnostics will in future gain greater importance and use in basic and applied research and in industrial applications than conventional electrochemical methods.

A completely new age of inhibitor research started with the development of scanning tunnelling probes at the end of the 1980s/beginning of the 1990s. With STM, AFM and related probes (also including electrochemistry), it became possible to investigate interface reactions and surface situations on an atomic scale. Exciting new views of corrosion inhibition were obtained. Also, many mechanisms that had only been postulated previously could now be proved with these new tools. For some applications, it is now possible to scan one picture of a small surface area at atomic resolution within less than 1/20 of a second, which makes it possible to view atomic and molecular processes on surfaces in real time, as in a movie. Such investigations again make it clear that interface reactions such as the corrosion of material and its inhibition can only be understood as 3D processes. Any idealisation into a 2D world would compromise the scientific insight into heterogeneous surface reactions.

As electrochemistry is only one, and very often not even the most important, part of the metal corrosion reactions, many non-electrochemical tools have been applied in recent decades in order to improve the understanding of corrosion processes and options for the protection of materials. Specifically, spectroscopic methods, with their year-by-year increase in accuracy and sensitivity, have contributed much: for example, ion scattering spectroscopy, secondary ion mass spectroscopy (SIMS) instrumentation [specifically time-of-flight (TOF)-SIMS], infrared (IR) spectroscopy, Fourier transform IR reflection absorption spectroscopy and reflectance spectroscopy, (laser) Raman spectroscopy (applicable also as an *in situ* method), surface-enhanced Raman spectroscopy, second harmonic generation spectroscopy, X-ray photoelectron spectroscopy, Auger electron spectroscopy, electron spectroscopy for chemical analysis, laser micromass analysis, and temperature-programmed desorption mass spectroscopy. Other methods that have proved very helpful in developing a mechanistic understanding of inhibition reactions include the (electrochemical) quartz crystal microbalance, ellipsometry, X-ray diffraction, and low-energy electron diffraction.

2.10 Final comments

The use of corrosion inhibitors is one option for preventing corrosion failures of metals. It is a simple and low-cost routine method in a great number of industrial fields, and in many applications has no real alternatives. The principles of corrosion inhibition are widely understood, and this understanding has led to the discovery of a vast number of chemical compounds that are active and highly efficient, even under severe environmental conditions.

However, it has been realised over the years that chemicals which are highly efficient corrosion inhibitors may impair the quality of the environment and may present hazards for human, animal and plant life. This led to legal constraints on the use of inhibitory substances, and challenged scientists to find alternatives or substitutes that are more environmentally friendly and, additionally, may be more efficient at lower concentrations and lower cost. In some cases, it was possible to fulfil the demands; in others, not all aims could be achieved. This leaves the field open for future research activities.

However, as already outlined, this research also encounters constraints and handicaps due to environmental concerns and legal restrictions. This is because ‘new’ chemicals and sometimes even ‘old’ chemicals have to be tested at very high cost for their environmental impact in water, on land and in the air. Even if a new compound were to be found that improved the present situation in the field of application, the monetary burden of legally demanded tests would hamper its adoption by industry. The use of old compounds in new applications could be one route of future research.

Another route would aim at achieving better analytical control of inhibitor concentrations. Analysing the concentration of corrosion inhibitor additives in industrial systems has been a problem for decades. One reason is that industrially used inhibitors are generally not pure substances and, additionally, are a mixture of different generic classes of substances. All of this makes the analysis difficult. To analyse only for a tracer substance may be dangerous, because of the possibility of selective adsorption and absorption. On the other hand, it was generally not in the interests of the inhibitor supplier for the customer to be able to analyse the inhibitor package. This could lead to an unwanted transfer of knowledge and could produce undesired competitive situations.

However, it has become an essential part of risk management and maintenance in industrial plants to identify primary risk factors and take countermeasures in order to increase the availability and integrity of the plants. As the availability of a corrosion inhibitor may be an essential risk factor, monitoring of inhibitor availability, i.e. real-time monitoring of inhibitor concentration, will become an important and essential demand from the plant operator to the inhibitor supplier. This needs a revisiting of inhibitor formulations and tailored design of chemical structures that have multifunctionality in service applications, and – in addition to high inhibitory efficiency – are easy to analyse by simple and field-hardened online methods. This is an interesting field for academic and applied research.

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3

The past, the present and the future of high temperature corrosion research – an EFC view

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3.1 Introduction

For the average person, high-temperature corrosion is an unknown factor in daily life, since the consequences of high-temperature corrosion are usually not obvious. The reason is that high-temperature corrosion occurs behind walls, as high-temperature processes are usually shielded from their environment. However, this type of corrosion can be lifetime- and performance-determining in a number of everyday examples, e.g. automotive engines (exhaust parts, catalyst carriers), jet engines, household heating systems, energy conversion systems (fossil power stations), and petrochemical and chemical process industries. Most of these applications became of technical importance at the end of the 19th century and the beginning of the 20th century, which is the reason why (as will be shown later) high-temperature corrosion only started to appear in the literature at that time. It was in particular in the second half of the 20th century when high-temperature corrosion research became a major key to increasing efficiency and reliability in the industrial areas mentioned above, and due to ambitious requirements in high-temperature operation following demands for even higher efficiencies and lower emissions of environmentally hazardous compounds, research in this field is still characterised by dynamic development.

The topic of high-temperature corrosion has been part of the work of the European Federation of Corrosion (EFC) for about 40 years. As the EFC celebrated its 50th anniversary in 2005, this was an opportunity to look back on the history of high-temperature corrosion and on its role in the activities of the EFC. Furthermore, this was an occasion to reflect on the present developments in the field and, where possible, on those of the near future. The aim of this paper is to underline the role of high-temperature corrosion research for established and advanced technologies and also to provide an eye-opener as to how much basic understanding had already been achieved in the very first years of research in this field.

3.2 History

As a common approach today to find out about the history of a technological development, an Internet search can be very useful. If one uses this approach for high-temperature corrosion, the results can be rather frustrating, and it is actually only if one searches by the keyword ‘corrosion’ that some more or less satisfactory information can be found. This situation is also very much illustrated by the ‘timeline of corrosion history’ [1], which is given in Table 3.1. While the first citation, dealing with protection against aqueous corrosion (a type of corrosion which, of course, is much more obvious in daily life), dates back to 412 BC, the first reference to high-temperature corrosion in this list is found for the year 1913. A more detailed search beyond the historical compilation in Table 3.1 reveals that high-temperature corrosion already played a role in much earlier times, and one nice example is the Chimú

Table 3.1 Timeline of corrosion history [1], presenting some historical landmarks of discoveries related to the understanding and management of corrosion.

Date	Landmark	Source
412 BC	Antifouling paint	Unknown
1675	Mechanical origin of corrosiveness and ‘corrodibility’	Boyle
1763	‘Bimetallic corrosion’	HMS Alarm report
1788	Water becomes alkaline during corrosion of iron	Austin
1791	Copper–iron electrolytic galvanic coupling	Galvani
1819	Insight into electrochemical nature of corrosion	Thenard
1824	Cathodic protection of Cu by Zn or Fe	Sir Humphrey Davy
1830	Microstructural aspect of corrosion (Zn)	De la Rive
1834–40	Relationships between chemical action and generation of electric currents	Faraday
1836	Passivity of iron	Faraday, Schoenbein
1904	Hydrogen overvoltage as a function of current	Tafel
1905	Carbonic and other acids are not essential for the corrosion of iron	Dunstan, Jowett, Goulding Tilden
1907	Oxygen action as cathodic stimulator	Walker, Cederholm
1908–1910	Compilation of corrosion rates in different media	Heyn, Bauer
1910	Inhibitive paint	Cushman, Gardner
1913	Study of high-temperature oxidation kinetics of tungsten	Langmuir
1916	Differential aeration currents	Aston
1920–3	‘Season-cracking’ of brass = intergranular corrosion	Moore, Beckinsale
1923	High-temperature formation of oxides	Pilling, Bedworth
1924	Galvanic corrosion	Whitman, Russell
1930–1931	Subscaling or ‘internal corrosion’	Smith
1933	Probabilistic nature of corrosion	Evans
1931–9	Quantitative and electrochemical nature of corrosion	Evans
1938	Anodic and cathodic inhibitors	Chyzewski, Evans
1938	E-pH thermodynamic diagrams	Pourbaix
1950	Self-accelerating (autocatalytic) nature of localised corrosion	Uhlig
1956	Tafel extrapolation for measurement of kinetic parameters	Stern, Geary
1968	Electrochemical noise signature of corrosion	Iverson
1970	Electrochemical impedance spectroscopy (EIS)	Epelboin

culture in South America, which had its heyday between AD 1250 and AD 1460 [2,3]. In this culture, the Tumbago technique was developed; this used Au–Cu alloys (with up to 70% Cu) as a material that had the appearance of gold but avoided several of its drawbacks. These alloys had a lower melting point but a higher strength than gold. On heating in a simple furnace, selective oxidation of Cu took place on the surface, while the sub-surface became strongly enriched in Au. The process of selective oxidation combined with enrichment/depletion processes in the sub-surface zone is actually the key to the lifetime and performance of all today's technical alloys, and it was modelled in the first half of the 20th century (see later). The Tumbago technique, however, served for the production of a surface of pure gold on the less costly Au–Cu alloys when the copper oxide had been removed by rapid cooling (spalling of the oxide due to differences in the coefficients of thermal expansion of metal and oxide, an issue that, again, is of the highest importance for technical materials today) or by vegetal acid. Thus, the Chimú culture already used fundamental aspects of high-temperature corrosion for manufacturing components with optimised bulk and surface properties several hundred years ago, an approach that sounds quite familiar to those aiming at the development of processes for functional surfaces on alloys today.

In recent years, metal dusting as a corrosion mechanism has become of increasing interest in research; see, for example, [4]. However, the first report on coke deposition in an industrial process as the mechanism that may end up in metal dusting dates back to 1876 [5]. This paper describes in detail the situation in which 'carbonic oxide in the gas is decomposed with the ultimate formation of carbonic acid and solid carbon'.

The most spectacular example of high-temperature corrosion in the early days of chemical process industries, however, dates back to the beginning of the 20th century. In those days, the process of industrial ammonia production was developed, and for this process large amounts of high-pressure hydrogen had to be converted at elevated temperatures in the ammonia reactor. In extreme cases, these reactors, which were made from carbon steel, had lifetimes of little more than 3 days before they fractured due to dissolution of the strengthening carbides in the steel by the formation of methane from the carbides and hydrogen [6]. What remained was a porous spongy iron material without any mechanical strength. While today this type of high-temperature corrosion is suppressed by alloying the steels with strong carbide formers, e.g. Cr and Mo, in the old days a double-wall tube was used which consisted of an inner quasi-carbon-free mild steel tube that was not prone to high-temperature hydrogen attack and an outer wall of load-bearing high-strength carbon steel [6]. The latter, however, had been made pervious to hydrogen by a huge number of small holes, so that hydrogen that had diffused through the inner mild steel tube wall could escape into the environment without building up the critical pressures that are needed for this type of high-temperature corrosion.

The scientific discussion of high-temperature corrosion started in 1913, with a paper by Langmuir, who described the oxidation process of tungsten at low pressures [7]. He observed that oxidation of a metal can lead to a solid scale or a volatile species: 'A tungsten wire heated in oxygen at low pressure begins to oxidise at about 800 K, the oxide forming a brown or blue coating on the metal. By heating to about 1200 K the oxide volatilises without dissociation and leaves the wire clean and bright.' He also mentioned that electric charges have to be involved in the oxidation process ('the oxygen molecule, after taking up a negative charge, is held by electrostatic forces to the positively charged tungsten atoms and soon, by secondary reactions, combines with the tungsten and with oxygen atoms to form WO_3'), but admitted that 'the present experiments do not throw much light on the nature of these secondary reactions'.

The parabolic rate law of oxidation, which can be found in all textbooks on high-temperature corrosion, was first described by Tammann in 1920 [8]. In the somewhat exotic silver/iodine vapour system of his paper, the tarnishing layers on the metal grow according to the well-known rate law

$$\mathrm{d}y/\mathrm{d}t = p/y$$

or

$$y^2 = 2pt$$

where y is the layer thickness and p is a constant that is strongly related to the diffusion coefficient, D, of iodine in AgI. The iodine concentration gradient was described as

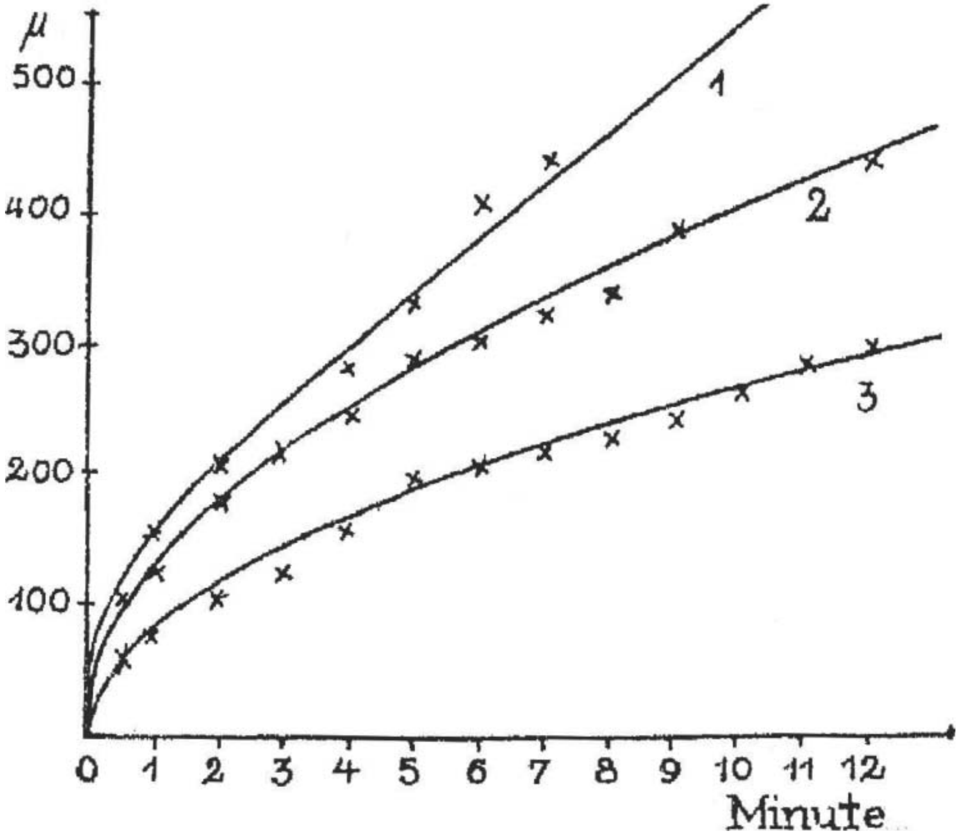
$$2p = aD\frac{dx}{dy}$$

where a is a correction factor. The results of Tammann's measurements are given in Fig. 3.1, which underlines the parabolic dependence of layer thickness on reaction time.

The first detailed scientific investigations of the oxidation of several metals in atmospheric oxygen were performed by Pilling and Bedworth [9] in 1923. They oxidised Cu, Ni, Fe, Zn, Pb, Cd, Ca and Mg, with the emphasis on the first three metals, and also confirmed the parabolic rate law for the reaction between oxygen and metal and for a number of oxidation times. Some of the sentences in their publication could be from a textbook of today:

> The transmission of oxygen through a compact oxide layer is accomplished (a) by the physical solution of oxygen in the solid oxide, (b) the diffusion of this dissolved oxygen from the exterior to the interior surface. The shape of the oxidation curve of the metal with a restraining oxide envelope can be derived without difficulty for a given concentration difference and . . . the rate of diffusion is inversely proportional to the length of the path of diffusion, in this case the thickness of the oxide layer. This is a parabolic curve, with the quantity of oxygen combining proportional to the square root of the time of oxidation. The above analysis refers, of course, to physically perfect oxide jackets . . .'

Figures 3.2 and 3.3 look rather familiar when one has read one of the common textbooks, such as that of Kofstad [10]. The most well-known results of this paper, however, are those listed in Table 3.2, which describes the volume change taking place when metal is converted into metal oxide. These values are commonly called the Pilling–Bedworth ratio, which is defined as the ratio of the volume of metal oxide produced by the reaction of metal and oxygen to the consumed metal volume. As a conclusion from this table, they distinguish between 'cellular or discontinuous-type oxides', where the ratio is less than 1, and 'compact or continuous-type oxides', where the ratio is greater than 1. As a general statement, they concluded that 'the group of metals forming cellular oxides comprises the majority of the so-called light metals; that of all of the heavy metals fall into the group of compact coatings'. The latter type of oxide was regarded as protective, and even today many of their findings are still

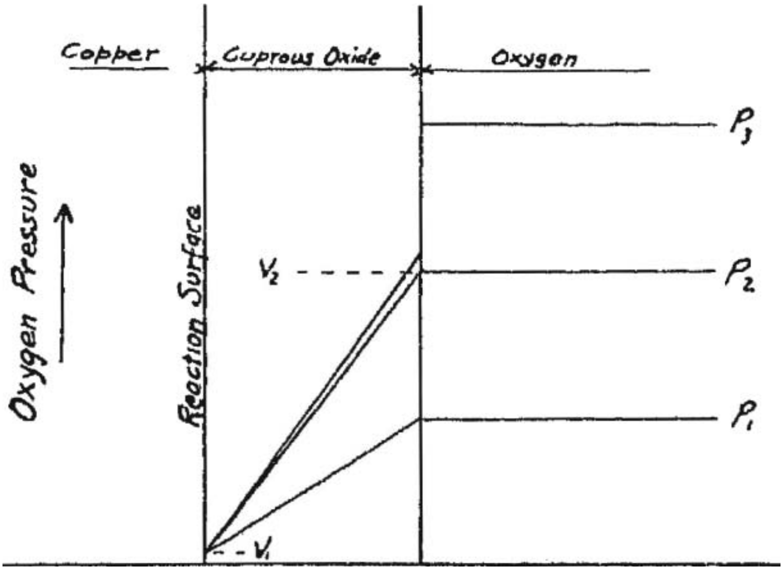


3.1 Kinetics of the growth of the tarnish layer on silver in iodine vapour, as observed by Tammann [8].

being used to explain the stress situation in oxide–metal systems [11], although some of these considerations can be misleading [12].

In 1926, Dunn analysed the work of Pilling and Bedworth in detail, and on the basis of his own experimental work, came to the conclusion that the parabolic law applies only to 'an oxide film whose properties remain constant in time' [13]. He furthermore realised the need 'to formulate a more fundamental theory of oxidation and diffusion'. In his paper, he outlined a theory of diffusion in solid solutions and deduced an expression for the variation of diffusion rate with temperature, based on the application of established laws to the thermal agitation of solids. The origin of a departure from the ideal parabolic law was traced by him to changes appearing in the oxide film during oxidation [14].

The Pilling–Bedworth work also stimulated investigations in Japan by Utida and Saito [15]. They oxidised a number of heating wires (Nichrome, Chromel, etc.), and found that after initial rapid oxidation, the rates may slow down dramatically once a protective oxide scale has formed. The oxidation rates, furthermore, depended on the

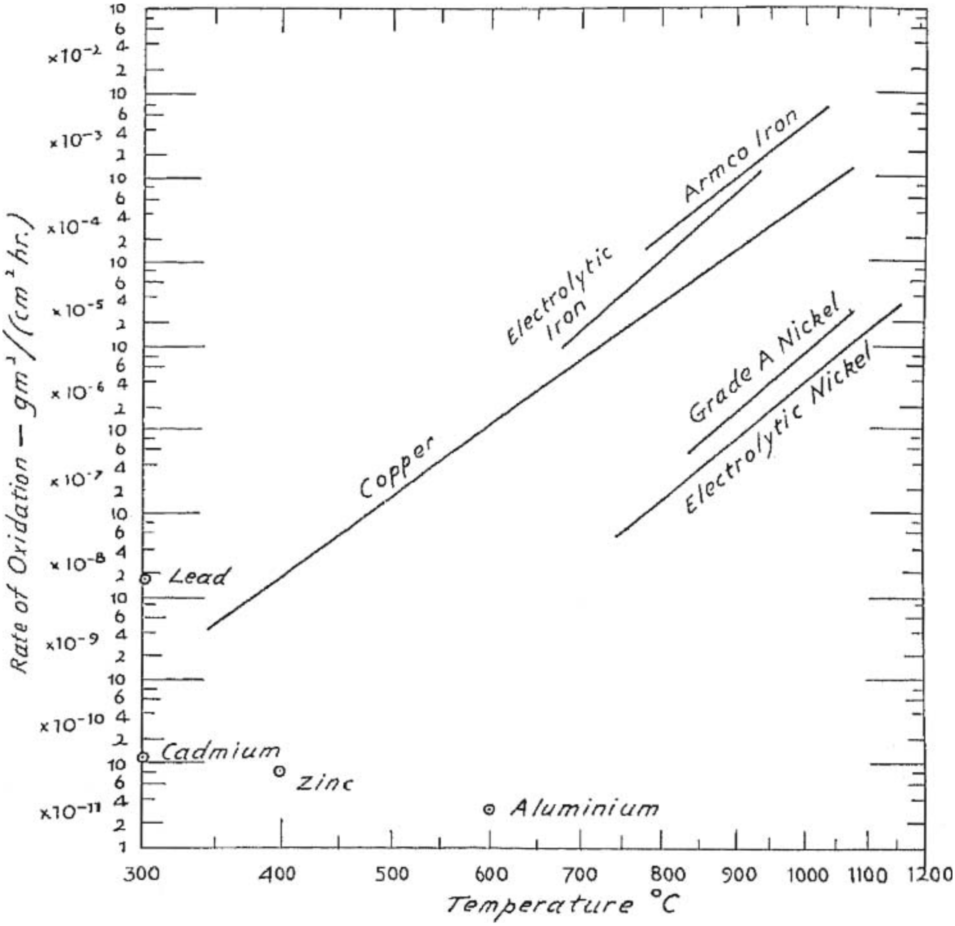


3.2 Oxygen partial pressure situation in a growing oxide–metal system, as described in [9].

amount of Fe in the alloy. The fact that after rapid initial oxidation much slower growth follows in a period of protection is typical of most of today's industrial high-temperature alloys.

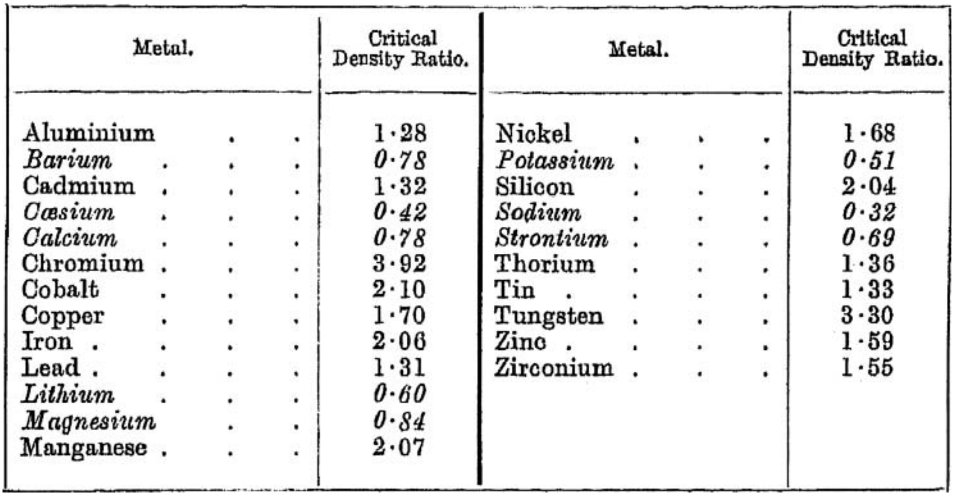
A significant part of the fundamentals of iron and steel oxidation was established by Pfeil in 1929 [16]. He described the appearance of three different oxide layers differing in structure and composition. 'With a few exceptions non-ferrous elements present in the iron before the oxidation are concentrated in the innermost of the three layers.' The mechanism of oxidation consists of 'counter-current diffusion – the iron diffusing outwards and the oxygen inwards through the scale . . .' This was concluded from the fact that 'foreign substances placed on the surface of the iron are not forced away by the formation of the scale, but remained unmoved and became completely enveloped by the scale'. Pfeil has, however, also become well known (possibly even better known) for his patent of 1935, which laid the grounds for the reactive element effect [17]. This patent describes how 'increased life is imparted by adding to the alloy one or more of the rare earth metals . . . in such a quantity that if there is any residue in the finished alloy it does not exceed 0.5%'.

Starting in 1933, a number of very significant contributions to the theory of oxidation of metals in alloys were published by Wagner, and these still form the most comprehensive theoretical basis, even in today's discussion of the mechanisms of high-temperature corrosion. Three key papers deserve mention here [18–20]. The first of these papers established the diffusion theory of oxide scales, the second analysed the situation of oxide scale nucleation and growth on binary alloys, and the third discussed the role of alloy composition and sub-surface zone depletion on the course of oxidation of alloys in a quantitative manner. The last of these papers was also the first in which the transition between internal oxidation and the formation of a continuous oxide layer was modelled.



3.3 Comparative oxidation rates of several metals (taken from [9])

Table 2. Critical density ratios from the original publication by Pilling and Bedworth (9)



Metal.	Critical Density Ratio.	Metal.	Critical Density Ratio.
Aluminium	1·28	Nickel	1·68
Barium	*0·78*	*Potassium*	*0·51*
Cadmium	1·32	Silicon	2·04
Cæsium	*0·42*	*Sodium*	*0·32*
Calcium	*0·78*	*Strontium*	*0·69*
Chromium	3·92	Thorium	1·36
Cobalt	2·10	Tin	1·33
Copper	1·70	Tungsten	3·30
Iron	2·06	Zinc	1·59
Lead	1·31	Zirconium	1·55
Lithium	*0·60*		
Magnesium	*0·84*		
Manganese	2·07		

There have been quite a number of other pioneering papers in the field that cannot be quoted here, due to space limitations. Only two more (perhaps arbitrarily chosen papers) will be briefly mentioned. In 1979, the importance of the role of mechanical aspects in high-temperature corrosion was pointed out very clearly in an overview paper [21], which stimulated a number of research projects in this field, some of which have been summarised in [12]. The other paper, which appeared in 1980, represents an excellent summary of the reactive element effect [22], which is one of the most important issues for increasing the resistance of technical alloys to oxidation at high temperatures.

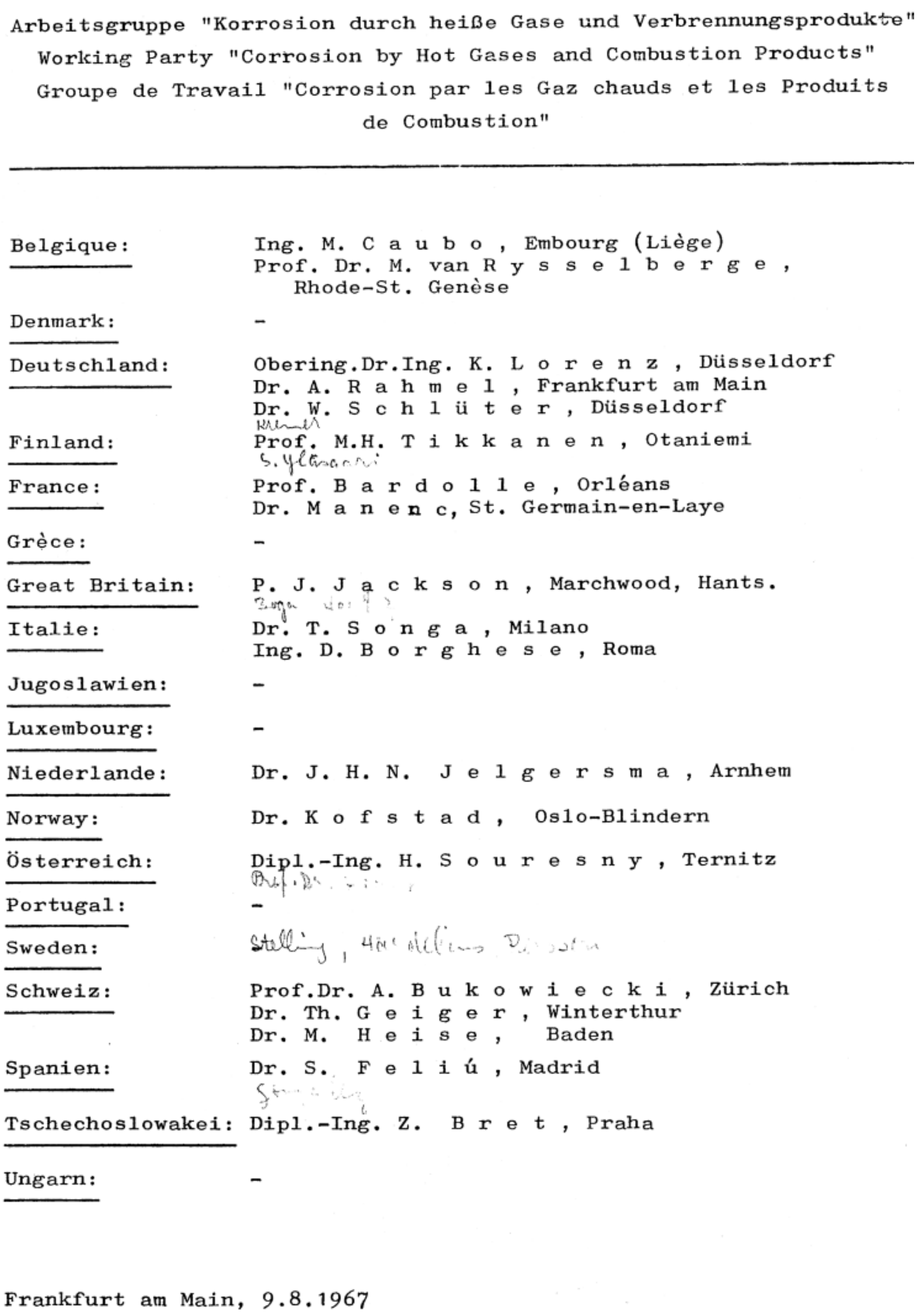
3.3 High-temperature corrosion in the EFC

The need to treat high-temperature corrosion issues as part of the EFC activities was identified in the early 1960s. At its meeting on 27 April 1965, the Board of Administrators initiated a foundation committee for a working party on high-temperature corrosion. On 11 November 1965, the foundation committee met in Frankfurt am Main and prepared a request to the national member societies to nominate candidates for a new working party by 1 March 1966. Evidently things went quite slowly, and a reminder had to be sent out on 9 August 1967. This reminder had the effect that nomination letters could be sent out to the members of the new working party a little later, and the first official meeting took place on 17 October 1967 in Düsseldorf. The new working party was named Working Party 3 on Corrosion by Hot Gases and Combustion Products (WP3), and was chaired by Alfred Rahmel until July 1986. The first members of WP3 are listed in Table 3.3.

The first task of WP3 was to draft a questionnaire in order to identify topics of interest among the member societies in this area. The questionnaire contained 18 topics from fundamental and applied research as well as from industrial applications. The evaluation of the replies was finished on 21 August 1969, and as a result a workshop on the role of trace elements in metals and alloys for the protection of steels was organised on 9–10 December 1970 in Düsseldorf. About 1 year earlier, a workshop on corrosion in molten salts had already taken place in Düsseldorf on 10–11 April 1969 under the auspices of the newly formed WP3. Until December 1970, the member society in charge of WP3 was the German Society of Iron and Steel-Makers (VDEh). In the framework of a reorganisation, the responsibility for WP3 was moved to DECHEMA, Frankfurt am Main. On 3 July 1986, Hans Grabke was appointed as the new chairman of WP3, and Michael Schütze joined him as the secretary. Hans Grabke led WP3 with great success until 1998. He organized a number of well-recognised workshops and sessions at EUROCORR conferences. After Hans Grabke's retirement, Michael Schütze was elected as the new chairman at EUROCORR 1998 in Utrecht. He continued the tradition, and now WP3 organises internationally recognised workshops on high-temperature corrosion every 2 years in Frankfurt and contributes a session to EUROCORR every year. The papers from these workshops and EUROCORR sessions have been published in the journals *Materials and Corrosion* and *Corrosion Engineering Science and Technology*, as well as in the form of books in the green EFC Series [23–27].

Since there has always been a lack of test standards, despite the industrial importance of the field, WP3 has taken over a leading role in the development of ISO guidelines. The first step as a follow-up of an EFC workshop on cyclic oxidation testing [24] was to initiate a European research project on the development of guidelines

Table 3.3 The first members of Working Party 3 after its foundation in 1967



Arbeitsgruppe "Korrosion durch heiße Gase und Verbrennungsprodukte"
Working Party "Corrosion by Hot Gases and Combustion Products"
Groupe de Travail "Corrosion par les Gaz chauds et les Produits de Combustion"

Belgique:	Ing. M. Caubo, Embourg (Liège) Prof. Dr. M. van Rysselberge, Rhode-St. Genèse
Denmark:	-
Deutschland:	Obering.Dr.Ing. K. Lorenz, Düsseldorf Dr. A. Rahmel, Frankfurt am Main Dr. W. Schlüter, Düsseldorf [illegible]
Finland:	Prof. M.H. Tikkanen, Otaniemi S. Ylasaari
France:	Prof. Bardolle, Orléans Dr. Manenc, St. Germain-en-Laye
Grèce:	-
Great Britain:	P. J. Jackson, Marchwood, Hants. [illegible]
Italie:	Dr. T. Songa, Milano Ing. D. Borghese, Roma
Jugoslawien:	-
Luxembourg:	-
Niederlande:	Dr. J. H. N. Jelgersma, Arnhem
Norway:	Dr. Kofstad, Oslo-Blindern
Österreich:	Dipl.-Ing. H. Souresny, Ternitz Prof. Dr. [illegible]
Portugal:	-
Sweden:	Stelling, [illegible]
Schweiz:	Prof.Dr. A. Bukowiecki, Zürich Dr. Th. Geiger, Winterthur Dr. M. Heise, Baden [illegible]
Spanien:	Dr. S. Feliú, Madrid [illegible]
Tschechoslowakei:	Dipl.-Ing. Z. Bret, Praha
Ungarn:	-

Frankfurt am Main, 9.8.1967

Table 3.4 Work items of Working Group 13 on High Temperature Corrosion of ISO Technical Committee 156 Corrosion of Metals and Alloys

Work item	Status
Continuous and discontinuous isothermal oxidation testing	Voting on CD
General guidelines for post-exposure examination	Voting on NWIP
Thermal cyclic oxidation testing	Voting on NWIP
Method of electrochemical corrosion test for metallic materials in molten salts	Submitted as NWIP
Method of dipping and embedding test in molten salt for metallic materials	Submitted as NWIP

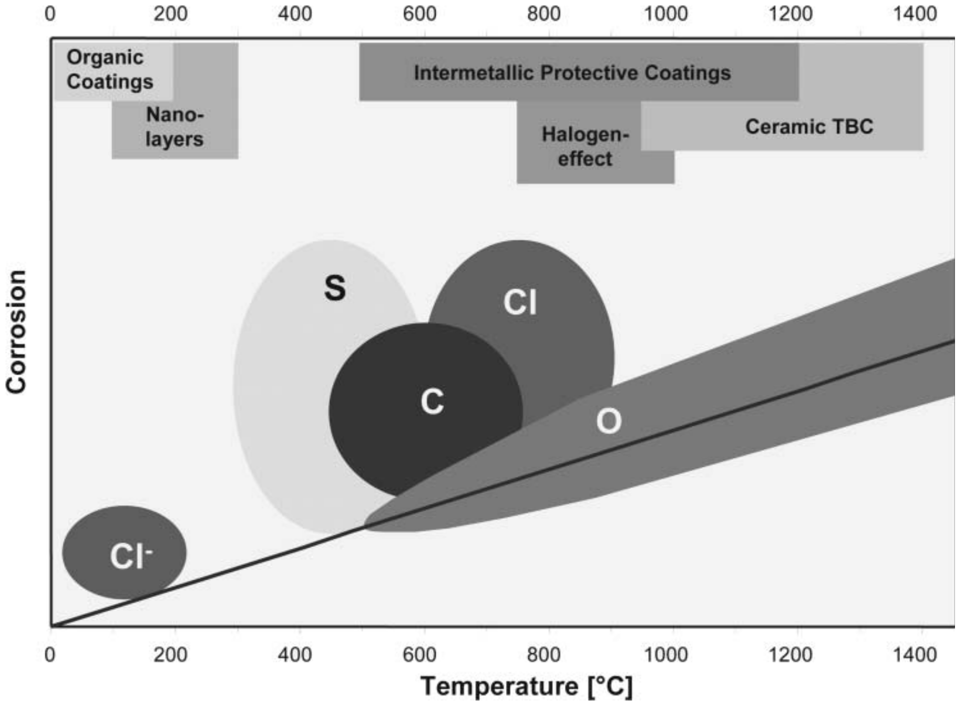
CD, committee draft; NWIP, new work item proposal (status February 2006).

for cyclic oxidation testing in 2001. This project included 23 partners from industry and academia, based in 11 European countries. The work ended in January 2005, and the draft guidelines developed were submitted to ISO as a work item. In the meantime, five work items are on the list of Work Group 13 on High Temperature Corrosion (WG13) of ISO Technical Committee (TC) 156 Corrosion of Metals and Alloys (Table 3.4), where the convenor is the chairman of WP3 and several members of this EFC working party are also members of the ISO TC 156 WG13. One of the major tasks of WP3 in the future will therefore also be to take care of proper standardisation activities in high-temperature corrosion in collaboration with colleagues outside Europe. Another main task of WP3 will be the collection and dissemination of knowledge in the form of workshops and publications.

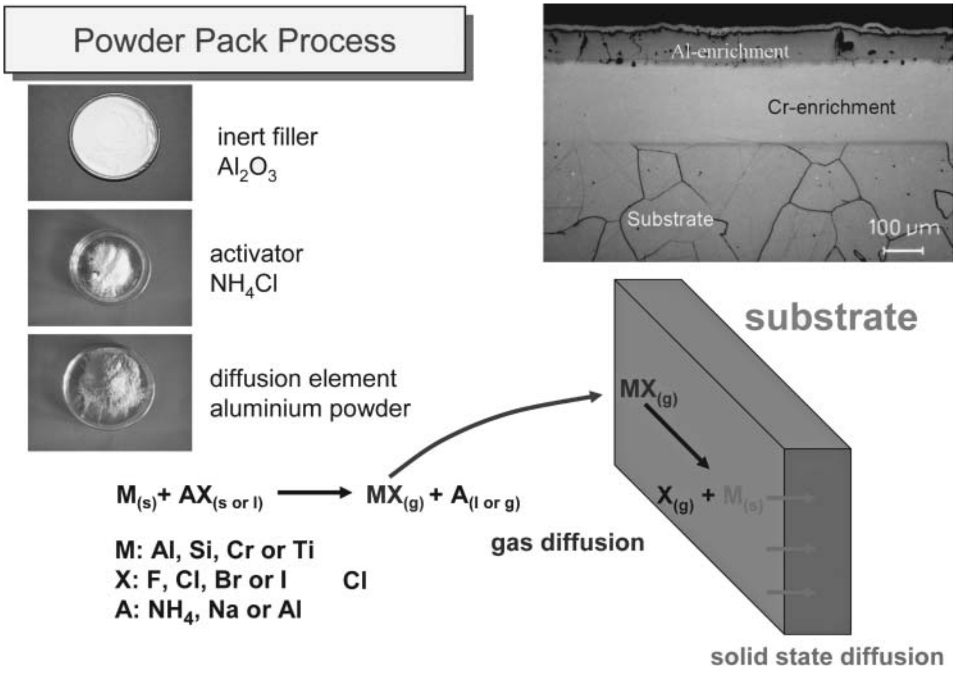
3.4 The situation of high-temperature corrosion research today

In the established technologies, high-temperature corrosion no longer seems to be a significant hazard as long as the existing knowledge is applied properly. Nevertheless, cases of damage are observed from time to time, due to unexpected operating conditions or improper selection of materials. In the meantime, a number of new high-temperature processes have been developed, or the operating conditions have shifted to more critical situations, due to changes in the operating environments or temperatures, mainly as a consequence of demands for higher efficiencies, the exploitation of energy-containing waste or critical fuels, and a decrease in polluting exhaust gases. Figure 3.4 summarises in a simple schematic diagram the temperature ranges and the extent of corrosion for several corrosive species in industrial applications.

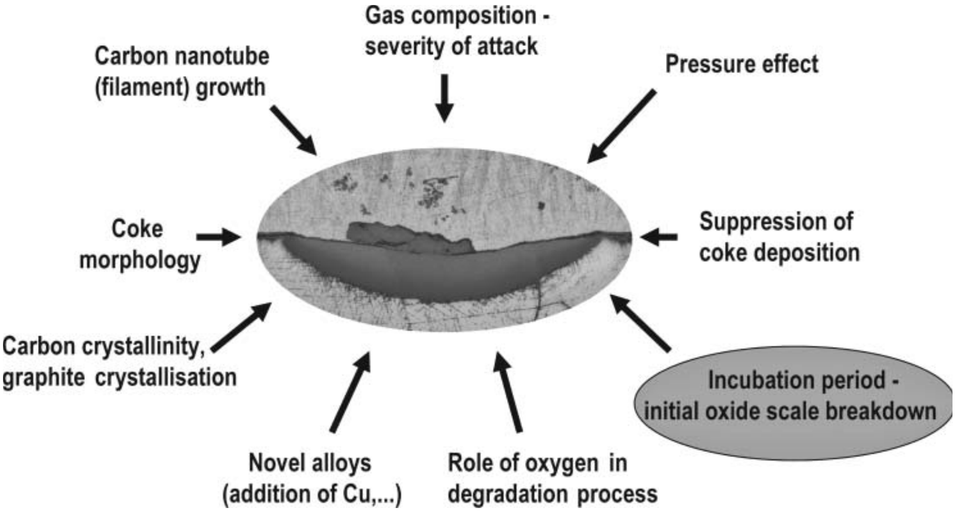
Figure 3.4 also shows the protection strategies at the different temperatures that nowadays dominate in high-temperature corrosion research, while the investigation of the corrosion mechanisms has assumed a secondary role. Since most of the industrial alloys, however, have come close to an optimum composition and structure, and further alloy modifications aiming at improved high-temperature corrosion resistance would degrade the mechanical and welding properties, the focus is now on the development of advanced coatings on conventional materials. These are usually Al- and/or Cr-rich intermetallic coatings applied either as overlay or as diffusion coatings. An example of the latter is shown as a two-step two-phase pack cementation coating in Fig. 3.5, and recent developments include multi-element co-diffusion



3.4 Corrosive species, temperature ranges and extent of corrosion from these



3.5 Two-step diffusion coating prepared by the powder pack process

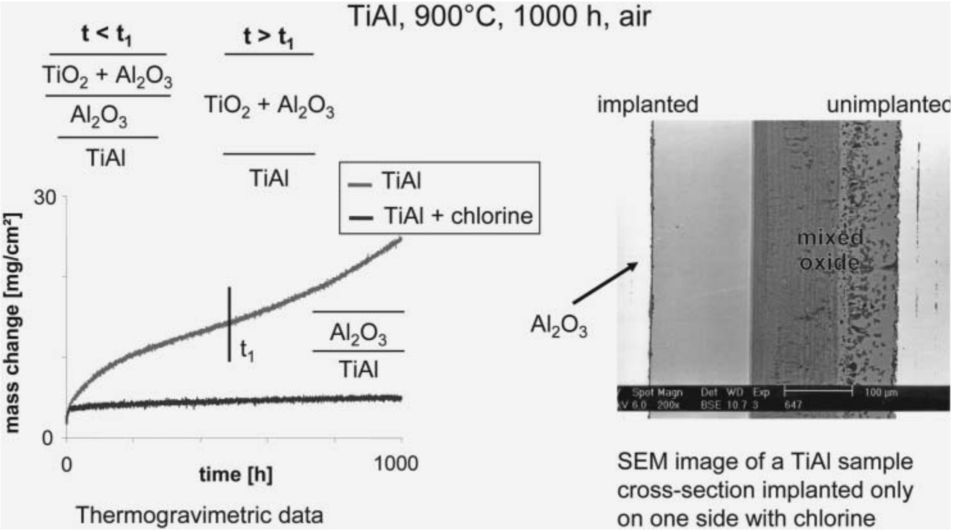


3.6 Current trends in metal dusting research

coatings with up to four elements with synergistic effects with regard to protection. Such coatings offer sufficient potential for protection in highly aggressive C-, Cl-, S- and/or V-containing high-temperature environments [28].

Even metal dusting is still a research area of significant interest (Fig. 3.6), where again the development of coatings for protection and the suppression of coke deposition has become the major focus.

Another issue where oxidation determines lifetime is ceramic thermal barrier coatings, which spall once the thermally grown oxide (TGO) between ceramic top coat and intermetallic bond coat has reached a critical state of ageing. Large research



3.7 The halogen effect on the oxidation resistance of Ti–Al alloys

Table 3.5 Programme of the Gordon Research Conference on High Temperature Corrosion in 2005

High Temperature Corrosion

July 24-29, 2005
Colby-Sawyer College, New London, NH
Chair: **Brian M Gleeson,** *Vice Chair:* **W J Quadakkers**

Metallurgical Factors Affecting Alloy Oxidation

John Perepezko, University of Wisconsin-Madison
"Oxidation behavior of multi-phase Mo-Si-B alloys and coatings"

Michael Brady, Oak Ridge National Laboratory
"Multi-component/multi-phase alloys as precursors to protective/functional surfaces via gas reactions"

Metal Dusting

Michael Schütze, Karl Winnacker Institut der DECHEMA
"Investigation of the initial stages in the metal dusting process"

David Young, University of New South Wales
"Metal dusting reactions: mechanisms and interventions"

Early Stages of Oxidation and the Nature of the Metal/Oxide Interface

Yannick Cadoret, ONERA
"Effect of platinum and sulfur on the high-temperature oxidation of NiAl"

Thermal Barrier Coating Systems

Wim Sloof, Delft University of Technology
“Microstructural and kinetic aspects associated with the initial oxide grown on MCrAlY-type bond coatings”

Wolfgang Braue, German Aerospace Center (DLR)
"Phase relationships and defect structure during oxide formation and growth in NiCoCrAlY- and PtAl-based TBC systems"

Xiao-gang Wang, Delphi
"Assessment of Ni(Al)/Al_2O_3 Interfacial adhesion using first principles calculations"

Modeling of Degradation Processes

Dan Renusch, Karl Winnacker Institut der DECHEMA
"Interacting spallation mechanisms and lifetime prediction of ceramic thermal barrier coatings"

Ulrich Krupp, University of Siegen
"Modeling of internal corrosion processes: challenges and limitations"

Compositional and Geometrical Factors Affecting Scaling Kinetics and Scale Breakdown

Dmitry Naumenko, Research Center Jülich
"Effect of minor elements on the microstructure and growth kinetics of alumina scales on FeCrAl-alloys"

Secondary Effects During Oxidation in Dry and Wet Environments

Prabhakar Singh, Pacific Northwest Laboratory
"Possible mechanisms associated with the accelerated corrosion of metals and alloys under bi-polar exposure (H_2-H_2O / metal / air) conditions"

Toshio Maruyama, Tokyo Institute of Technology
"Quantitative prediction of void formation in a thermally grown scale"

Accelerated Degradation in the Presence of Molten Oxidants

Carlos Levi , University of California, Santa Barbara
"Thermochemical degradation of thermal barrier coatings by molten deposits"

John Nicholls, Cranfield University
"Design of coating systems for aggressive, high-temperature environments"

Thursday Evening Talk

David Douglass, University of Arizona
"Minerals and materials science - many questions, few answers"

efforts are therefore being undertaken by the jet engine industries and the manufacturers of land-based gas turbines to develop lifetime models based on TGO parameters [29]. Last but not least, new material classes have been developed whose oxidation/high-temperature corrosion behaviour is not well known and that require new methods of protection. As an example, a new class of high-temperature lightweight alloys based on the stoichiometric compounds TiAl and Ti_3Al can be mentioned; these show an oxidation behaviour that is very different from what would be expected on the basis of traditional understanding [30]. Even a content of about 50% Al is not sufficient to establish a pure alumina scale in air at high temperatures. Rather, a mixed non-protective fast-growing TiO_2/Al_2O_3 scale is formed, which limits the use of these materials from an oxidation point of view to about 750°C. However, a surprising effect – the so-called halogen effect – can change the oxidation mechanism in such a way that only Al_2O_3 is formed on the surface, even up to temperatures of 1050°C, thus extending the use of this group of materials dramatically. This can be seen in Fig. 3.7, in which the oxidation rates of TiAl surfaces both implanted with halogen and in the original state, without implantation, are compared. The implantation or addition of a small dose of halogens affects the oxidation mechanism in a way that is now understood [31]; the formation of non-protective, fast-growing TiO_2 is suppressed, while the formation of Al_2O_3 is favoured.

3.5 Outlook

It would be presumptuous to claim to be able to provide a comprehensive outlook on the future development of high-temperature corrosion research. Therefore, it is not intended to make such an attempt here. However, a good impression of the present hot topics can be obtained from the programmes of the biannual Gordon Research Conference on High Temperature Corrosion, e.g. the one that took place on 24–29 July 2005 in New London, New Hampshire, which was chaired by Brian Gleeson. The programme is listed in Table 3.5, and shows that it is also the small increments on the way to new knowledge that characterise the activities of the community. One need not be a prophet to say that much of the development mentioned in the last paragraph has not yet reached perfection, a situation that will keep scientists and technicians busy for a while. It can, however, be suspected that high-temperature corrosion research will also be used more and more to explore new ways of manufacturing multifunctional surfaces. At least, at present, such development has started at several laboratories.

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4

Fifty years of nuclear corrosion in Europe: from the pioneering period to a safe and mature industry

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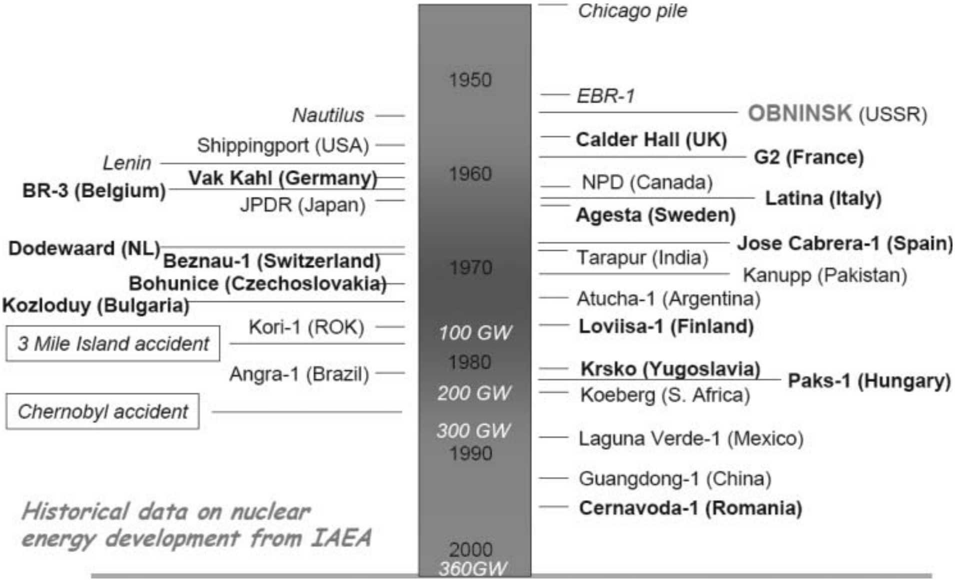
The discovery of radioactivity by Pierre and Marie Curie at the beginning of the 20th century had wide ramifications, leading to large advances and changes in areas as different as defence, medicine and energy production. Just after World War II, the military development of nuclear submarines had important implications for power generation, as they use pressurised water reactors (PWRs), first used in the US Nautilus submarine, which were to become the most widely used type in civil nuclear power. The first nuclear power plant (NPP) was connected to the national power grid in the Soviet Union, at Obninsk in 1954. It was a reactor of the RBMK type (a water-cooled reactor fuelled with natural uranium and with graphite as the moderator). This type of reactor has never been developed in the West, as it was not considered safe: the reactor that exploded at Chernobyl in 1986 was an RBMK.

However, at the end of the 1950s and in the 1960s, nuclear power generation had a flying start, as shown in the timeline of the first industrial NPPs (Fig. 4.1).

- In 1954, the UK Atomic Energy Authority (UKAEA) was set up for the development of nuclear technology, and 2 years later, the Calder Hall reactor was connected to the UK power grid. It was a Magnox prototype, which was fuelled by unenriched uranium metal and used magnesium alloy as the cladding material.
- In 1946, the Atomic Energy Commission in the USA initiated a development programme for nuclear power reactors that led to the first power plant, a PWR, operated by a private company (the Dusquesne Light Company) in 1957 at Shippingport.
- In 1945, the Commissariat à l'Energie Atomique (CEA) was created in France, and developed its own graphite-gas reactor (UNGC type), which used natural uranium, and fuel cladding made from a magnesium–zirconium alloy. The first UNGC reactor to go on-line was G-2 in Marcoule in 1959.
- The first nuclear power reactors were implemented in many European countries as shown in Fig. 4.1; Germany, Belgium, Italy, Sweden, Spain, The Netherlands, Switzerland, Czechoslovakia, Bulgaria and Finland all had one or more nuclear power reactors connected to the national grid before the end of the 1970s.

It was during that pioneering period that nuclear technology for peaceful purposes was largely developed. It was also during those pioneering days for nuclear energy

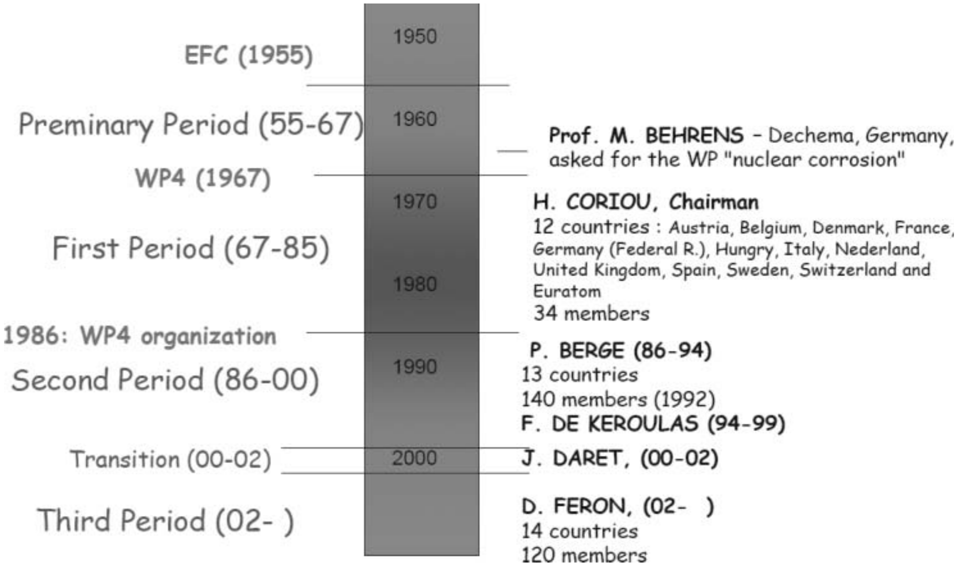


4.1 Timeline of the first industrial nuclear power plants *(italics are used for main events: nuclear submarines and accidents)*

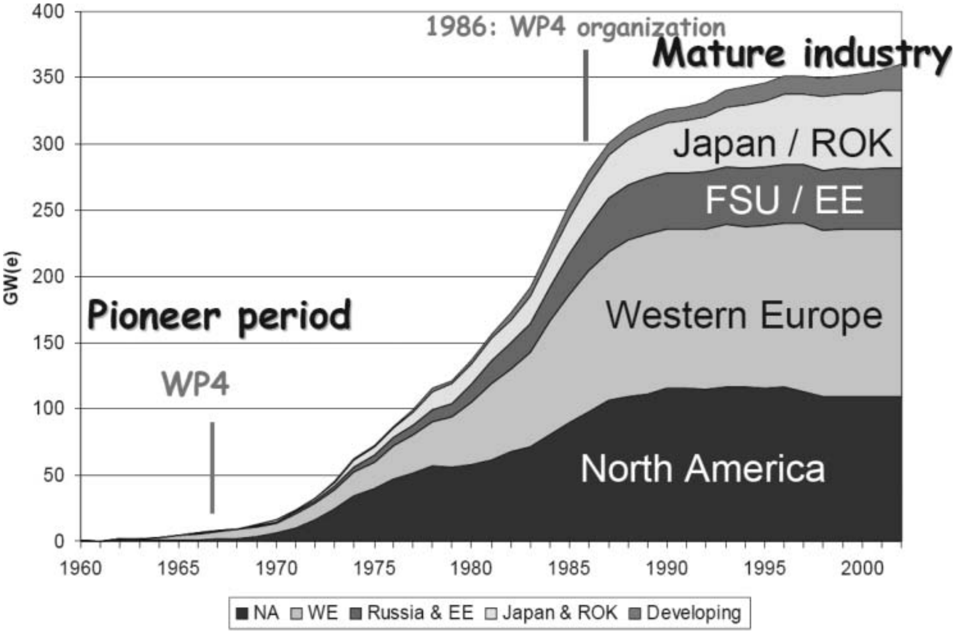
that the European Federation of Corrosion (EFC) was created (1955). In Europe, the treaty establishing the European Atomic Energy Community (Euratom) was signed in Rome in 1957, and led to a great deal of scientific and technical exchange and cooperation between the signatory founding states (Belgium, France, Germany, Italy, Luxembourg, and The Netherlands). Materials issues were key points in nuclear technologies, not only for NPPs, but also for all civil nuclear activities, from uranium enrichment (UF_6 is quite aggressive) to nuclear waste reprocessing, where materials have to resist nitric acid at high temperatures and high concentrations. International exchanges were important, and mainly on Euratom or bi-national bases. In 1965, Professor H. Behrens (DECHEMA, Germany) asked Henri Coriou, head of the corrosion department at the CEA, to create EFC Working Party 4 on Nuclear Corrosion (WP4), which was officially established in 1967, with 12 countries: Austria, Belgium, Denmark, France, Germany (Federal Republic), Hungary, Italy, The Netherlands, Spain, Sweden, Switzerland and UK. Euratom was also affiliated to WP4 (Fig. 4.2). During the first 20 years, WP4 was mainly organised like a 'private club', with one meeting each year, speeches on relevant items, free discussions and oral exchanges, but no reports and no minutes. It is also noteworthy that up to 1986, all meetings of WP4 were conducted in French (one of the three official languages of the EFC, with English and German). Good food and good wines were generally provided by the host country of the meeting.

There was good organisation during that pioneering period, but, as shown in Fig. 4.3, global nuclear capacity was increasing fast in Europe, Japan and the USA. During the mid-1980s, the nuclear industry in these countries was becoming a mature industry.

When Henry Coriou retired, Philippe Berge (EdF) was elected to chair WP4, and a new period of major development in WP4 began (Fig. 4.4).

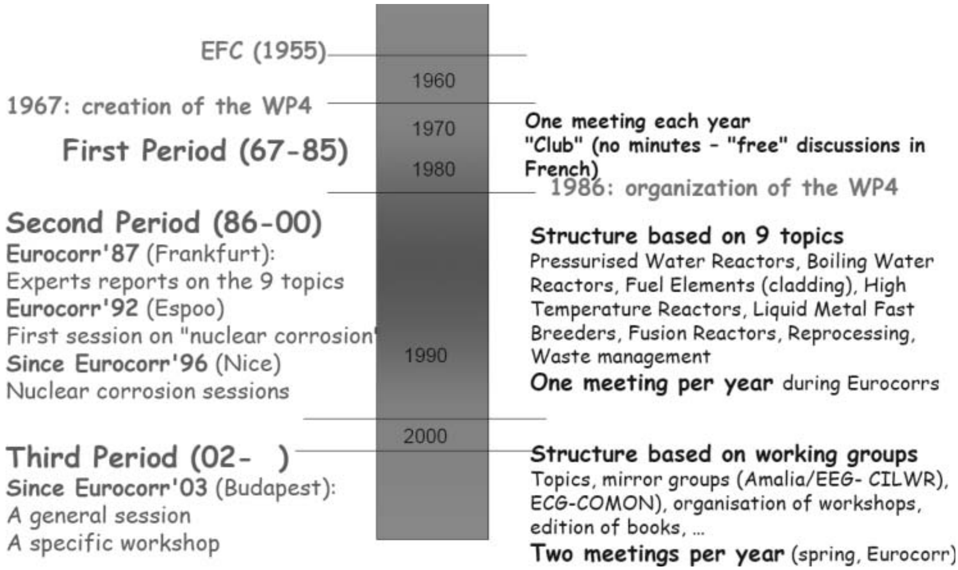


4.2 Timeline of EFC Working Party 4 Nuclear Corrosion, showing chairmen terms



4.3 Evolution of global nuclear capacity (data and curve from IAEA)

During his chairmanship, which encompassed nearly 10 years (1986–1994), Philippe Berge introduced, with Gérard Pinard-Legry (CEA) as secretary of WP4, great changes that were in accordance with the new challenges facing the nuclear industry: English became the exchange language inside WP4. Debates were opened to the scientific community. WP4 was structured into nine main topic areas where corrosion plays a major role: PWRs; boiling water reactors (BWRs); fuel elements (cladding);



4.4 Evolutions of the organizations of the European Federation of Corrosion (EFC) and of the Working Partry on Nuclear corrosion (WP4)

high-temperature reactors; liquid metal fast breeders; fusion reactors; reprocessing; and waste management. It is evident that even today these subjects are still very topical and important. During one of the first EUROCORR conferences, in Frankfurt (EUROCORR 1987), nuclear experts reported on each of the nine topics and decided that annual meetings of WP4 would in future take place in conjunction with EUROCORR. On the basis of their contributions, the very first book in the EFC Series of green books was produced. It is indicative of the dynamism of WP4 that EFC No. 1 should be a working party report on corrosion in the nuclear industry. The first workshop organised by WP4 was held in Switzerland, at Handeck in 1991 on ‘Corrosion problems related to nuclear waste storage’, and led to EFC No. 7, which for 10 years was the main source of reference for researchers and engineers addressing long-term corrosion for nuclear waste management. The first session on nuclear corrosion took place during EUROCORR 1992 in Espoo (Finland).

When François de Kéroulas (EdF) was elected as the new chairman of WP4 in 1994, with Gérard Santarini (CEA) as secretary, the working party had 140 members who were very active on various matters related to nuclear corrosion. It was then decided in Nice (EUROCORR 1996) to have a session on nuclear corrosion during each EUROCORR conference. The second workshop of the WP4 took place 10 years after the first one, and was co-organised by Damien Féron (CEA) and Digby Macdonald (State University of Pennsylvania, USA) at the ‘maison d’hôtes’ of the CEA centre at Cadarache in Provence (south of France), which is an old castle from the Middle Ages and was the ideal location for the subject: ‘Prediction of long-term corrosion behaviour in nuclear waste systems’.

After the chairmanships of François de Kéroulas (1994–2000) and of Jacques Daret (CEA, 2000–2002), Damien Féron (CEA) was elected as chairman of WP4 during EUROCORR 2003 in Budapest, with Yves Rouillon (EdF) as the scientific secretary (2000–2005), while Mylène Belgome (CEA) has been acting as secretary since 2003. Nearly 40 years after its foundation, and nearly 20 years after the reorganisation conducted by Philippe Berge, the revival of nuclear energy occurred in Europe, as shown, for instance, by: the construction of two new European prototype reactors in Finland and in France; by the decision to build the ITER machine (a fusion reactor) in Cadarache, France; and, in the world, with the new deal of 'Generation IV' (the roadmap of ten nations preparing today the nuclear energy of tomorrow). These developments in the nuclear environment led WP4 to adopt in Budapest (2003) an active 3-year plan in order to follow the nuclear 'renaissance' taking place at the beginning of the new millennium. The three main objectives were as follows:

- to provide links between European teams and EU-funded programmes in the nuclear corrosion field, with an opening onto the world;
- to initiate and stimulate opportunities for exchanges on scientific and technical subjects related to nuclear corrosion, particularly on today's main nuclear research areas: waste systems, water reactors, Generation IV and fusion reactors;
- to promote corrosion science and technical developments by events such as seminars, workshops, and publications.

Today, the organisation of WP4 is based on 11 task force groups:

1. Management (chairman, scientific secretary, secretary);
2. Corrosion and extension of the lifetime of existing power plants (D. Gomez Briceno, CIEMAT, Spain);
3. Prediction of long-term corrosion in nuclear waste repositories (B. Kursten, SCK-CEN, Belgium);
4. Concrete behaviour in NPP and waste facilities (in connection with the Nuclear Energy Agency, OCDE/NEA);
5. Electrochemistry at high temperatures (R.W. Bosch, SCK-CEN, Belgium);
6. Corrosion monitoring (A. Molander, Studsvik, Sweden and S. Ritter, PSI, Switzerland);
7. Corrosion of internals in light water reactors (LWRs) (R. Novotny, Petten, EU);
8. Microbially induced corrosion in NPPs (R. Killian, Areva NP, Germany);
9. Generation IV;
10. Corrosion issues in fusion facilities (G. Benamati, Italy);
11. Education – summer school(s).

Some have already been very active, with the organisation of internal meetings or open seminars (see below), either during EUROCORR conferences or as stand-alone events. Since the adoption of this plan, two WP4 meetings have taken place each year: a spring meeting at the beginning of the year, with only the WP4 members, and the autumn meeting during EUROCORR, where everybody is welcome.

Several seminars and workshops have been organised or are planned:

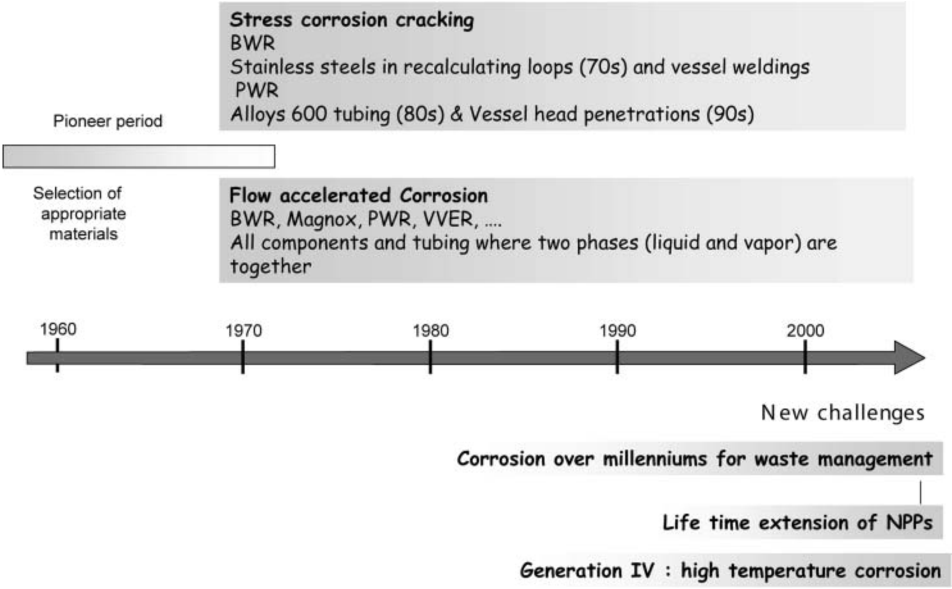
- during EUROCORR:
  - 2004: second workshop, 'Prediction of long term corrosion behaviour in nuclear waste systems';
  - 2005: workshop on 'Corrosion issues in future nuclear systems';
  - 2006: workshop on 'Corrosion issues in reprocessing plants';

  - 2007: two workshops, ‘Corrosion monitoring in nuclear systems’ and ‘Initiation of stress corrosion cracking in light water reactors (LWRs): focus on ageing and welds’;
- or in connection with national or European programmes:
  - 2004: EFC Event No. 279, ‘Electrochemistry in light water reactors’ (LIRES programme);
  - 2006: EFC Event No. 284, ‘Corrosion and long term performance of reinforced concrete in nuclear power plants and waste facilities’, in connection with OCDE/NEA (CIMETAL programme);
  - 3rd International Workshop on ‘Prediction of long term corrosion behaviour in nuclear waste systems’, Pennstate University, USA, 14–18 May, 2007 (EFC Event No. 301), with OCDE/NEA.

The relationship between WP4 and the OCDE/NEA (Nuclear Energy Agency) ought to be highlighted, since it contributes to the efficiency of WP4 and to its reputation.

Publications in the EFC Series, and with other publishers, have also been encouraged, as shown in the annex, where the WP4-sponsored publications are listed. The objective of publishing one book a year has been exceeded in recent years. The website of the EFC includes a section devoted to WP4, which includes the announcement of new events and new publications as well as the minutes of its meetings.

From the pioneering period to the new age of nuclear energy at the beginning of this millennium, the nuclear corrosion community has had to face many challenges (Fig. 4.5). In former days, the selection of appropriate materials was the major activity, as a wide range of media was encountered, from gaseous UF_6 for isotopic separation to concentrated nitric acid at high temperature for reprocessing plants. Perhaps, at that time, water reactors were not believed to have the most aggressive



4.5 Main corrosion challenges faced during the past 50 years in nuclear corrosion and future challenges environments. Nevertheless, corrosion in water reactors rapidly became one of the major concerns. Stress corrosion cracking has been one of the main challenges since almost the beginning of BWRs and also for PWRs. Even though the materials and the chemistries are not the same, through extensive research and collaboration, corrosion engineers and scientists have succeeded in mitigating these phenomena. All types of commercial reactor have experienced flow-accelerated corrosion, which also led to large research and redevelopment programmes and large-scale collaboration in Europe and beyond. Even though these phenomena are now under control, they are still major concerns for the life extension of NPPs.

The objective of extending the lifetime of many NPPs is an illustration of the generally good material selection and technological choices made by the nuclear community during the pioneering period. Lifetime extension is, nevertheless, one of the main challenges that the corrosion community has to face nowadays: it is necessary not only to have experimental data, but also to understand the mechanisms of the corrosion phenomena. Two other major challenges may be identified today: (a) the prediction of corrosion over millennia for nuclear waste management, which is a necessity for the safe storage of waste and for the acceptability of nuclear technology by the general population; and (b) the behaviour of materials at high temperatures in gas, liquid metals or molten salts for the new Generation IV reactors.

Nuclear power is part of the answer to the global energy challenge: to produce more energy while reducing CO_2 emissions. With its past experience, WP4 has the ambition to contribute to the success of this challenge.

We cannot close this short review of the activities of the 40-year-old WP4 without expressing gratitude to all its past and present members, who have achieved remarkable progress in the field of corrosion in nuclear technology. This was done in a perfect and friendly atmosphere of international cooperation, where there was no room for personal or national interest.

Annex: books published under the authority of WP4

In the EFC Series:

No. 1, *Corrosion in the Nuclear Industry*, 1989, Institute of Materials, London.

No. 7, *Corrosion Problems Related to Nuclear Waste Disposal*, 1991, Institute of Materials, London.

No. 36, *Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems*, 2002, Maney Publishing, London.

No. 48, *Corrosion of Metallic Heritage Artefacts: Investigation, Conservation and Prediction for Long Term Behaviour*, 2007, Woodhead Publishing Ltd., Cambridge.

No. 49, *Electrochemistry in Light Water Reactors: Focus on Reference Electrodes, Measurements, Corrosion and Tribo-corrosion Issues*, 2007, Woodhead Publishing Ltd., Cambridge.

No. 51, *Corrosion Issues in Light Water Reactors: Focus on Stress Corrosion Cracking and Practical Experience*, 2007, Woodhead Publishing Ltd., Cambridge.

In other series:

Proc. second workshop on 'Prediction of long term corrosion behaviour in nuclear waste systems'. ANDRA, 2005. Châtenay-Malabry, France.

Proc. workshop on 'Corrosion and long term performance of reinforced concrete in nuclear power plants and waste facilities', *J Physique* IV (136) (2006).

5

Corrosion Education – The contribution of the European Federation of Corrosion

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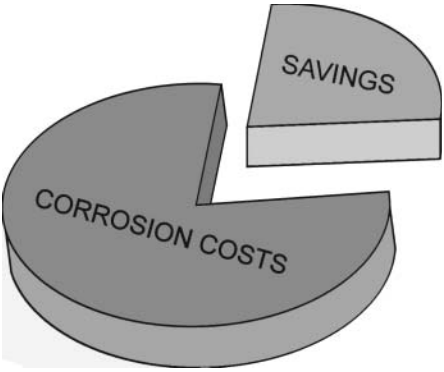
5.1 Introduction

Corrosion is recognised as one of the most serious problems in our modern society, and the resulting losses each year are in the hundreds of millions of euros. Cost-of-corrosion studies have been undertaken by several countries. These studies have ranged from formal and extensive efforts to informal and modest efforts, but the common finding has been that the annual corrosion costs ranged from approximately 1% to 5% of the gross national product of each nation. However, about 23% of these costs can be avoided by better use of currently available knowledge (Fig. 5.1), in accordance with the Report of the Hoar Committee [1].

Consequently, many present-day corrosion problems frequently arise from known causes, and are due to the affected sectors being uninformed regarding available remedies that would allow them to be avoided, or at least reduced. At present, corrosion science is increasingly developing interdisciplinary fields in which corrosion plays an essential role, and corrosion is also deeply involved in fundamental work related to various technologies. Corrosion education is one of the most effective ways of disseminating information on corrosion problems and on corrosion prevention measures. The training should provide a reasonable foundation in the diagnosis of corrosion problems and a working knowledge of corrosion control process. Conscious of this situation, European corrosion societies, though the European Federation of Corrosion (EFC), have taken the initiative of creating a working group interested in the problems of corrosion. Information on the roles played by this group is given here.

5.2 Working Party 7 on Corrosion Education

The EFC was stimulated to consider ways in which it could contribute to corrosion education at an international level. As a consequence of a proposal of representatives from member societies, Working Party 7 on Corrosion Education (WP7) was established after a decision of the General Assembly, Amsterdam, in 1969. Its first chairman was Mr E. B. Bergsman (Sweden). The subsequent chairmen were Mr G. Svendenius (Sweden), Professor J. S. L. Leach (UK), Professor D. Landolt (Switzerland), Professor J. M. Costa (Spain), and now, Professor R. A. Cottis (UK).

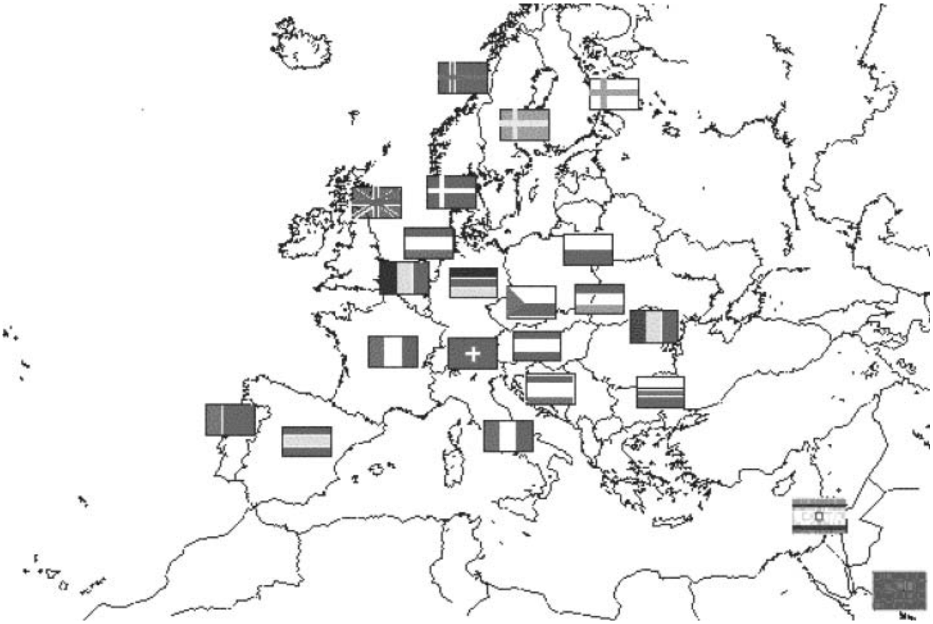


5.1 Corrosion costs and potential savings

Most of the WP7 members are university teachers engaged in corrosion, but some members come from advisory services, industry and government. At present, the group includes 43 members from the 22 countries shown in Fig. 5.2.

WP7 brings together experts in the field of corrosion for the regular exchange of ideas and experience and for joint work in the areas where there is a recognised need for development activities. Its aims include the provision of information on different approaches to disseminate understanding of corrosion, to discuss the problems involved, and to give examples of successful education.

The wide-ranging education and research activities of the members of WP7 provide an excellent basis for contributing to corrosion education; formal meetings take place at least once a year. The most important objective of these meetings is to provide opportunities for the interchange of opinions between participants; the



5.2 Countries represented in WP7

dialogue between them facilitates the development of their own ideas on corrosion education. The different methods and techniques available for such education, in terms of mechanism, methodology or content, are also examined.

In addition to education of corrosion specialists, efforts to a large extent are addressed to the provision of aids for the corrosion education of designers, maintenance engineers and plant supervisors and others who come into contact with corrosion prevention without being able to specialise in the subject.

Apart from the general objectives of WP7, the purpose of the group is to serve industry in all ways by which corrosion science can help foster international understanding. Cooperation with industry in the field of corrosion is especially important, and in recent years, WP7 has undertaken a very extensive task, together with the other groups involved (Fig. 5.3).

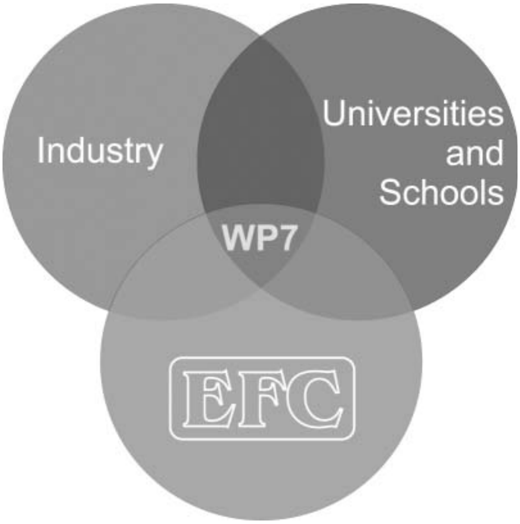
The main activities of WP7 involve:

- meetings on educational subjects
- compilation of information for those concerned with educational and training policy
- preparation of books and other educational aids
- courses arranged in collaboration with other institutions
- advice on certification
- dissemination of information for professionals for solving corrosion problems within their industrial activities

These have included learning to use technological tools dealing with social issues that are available to everyone.

5.3 Major activities

The work of WP7 forms the basis of much EFC activity, since it deals with encouraging shared effort in any training activity, providing a forum through which



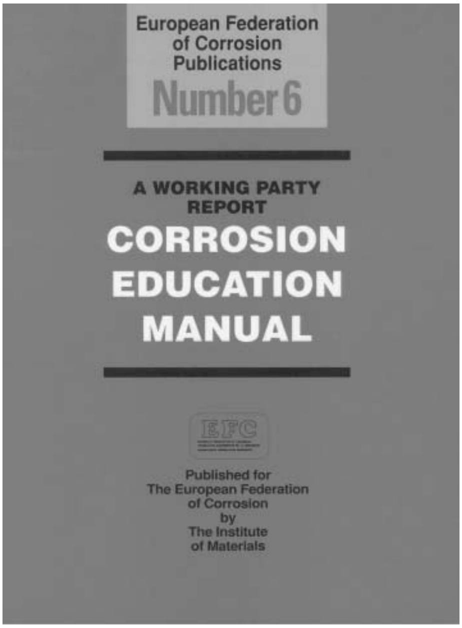
5.3 WP7 on Corrosion Education within the EFC significant reports, studies and experiments will be given wide circulation. The results of WP7 activities include a survey on aids for corrosion education in the member countries, several textbooks and films on corrosion, and other educational initiatives [2,3].

5.3.1 *Corrosion Education Manual*

WP7 decided to start its work by producing a *Corrosion Education Manual*. The first edition was coordinated by the staff of the Swedish Corrosion Institute. The book was intended as a useful tool for teachers and others looking for help with problems of corrosion education, showing where improvements in educational standards were needed. However, it provides sources of information for all those concerned with the science and technology of the protection of materials against corrosion. For teachers, it provides examples of courses and information on textbooks and other teachings aids; for students, it supplies information on textbooks, handbooks, journals and advisory services that should prove to be of value to their studies and subsequent careers; for designers, chemists, engineers and other professionals, it indicates sources of advice for solving corrosion problems within their industrial activities. Its first edition was published in 1972, and this was followed by revised editions, the last one being published by the Institute of Materials (IoM), London (Fig. 5.4). The latest revised and enlarged edition, under the title *Corrosion Education Sources*, prepared in accordance with proposals from WP7 members to improve the present contents, was produced in electronic form.

5.3.2 Educational films and videos

Many of the educational films produced are mainly for local use within a particular university or country, and when these materials are produced professionally, the



European Federation
of Corrosion
Publications
Number 6

A WORKING PARTY
REPORT
CORROSION
EDUCATION
MANUAL

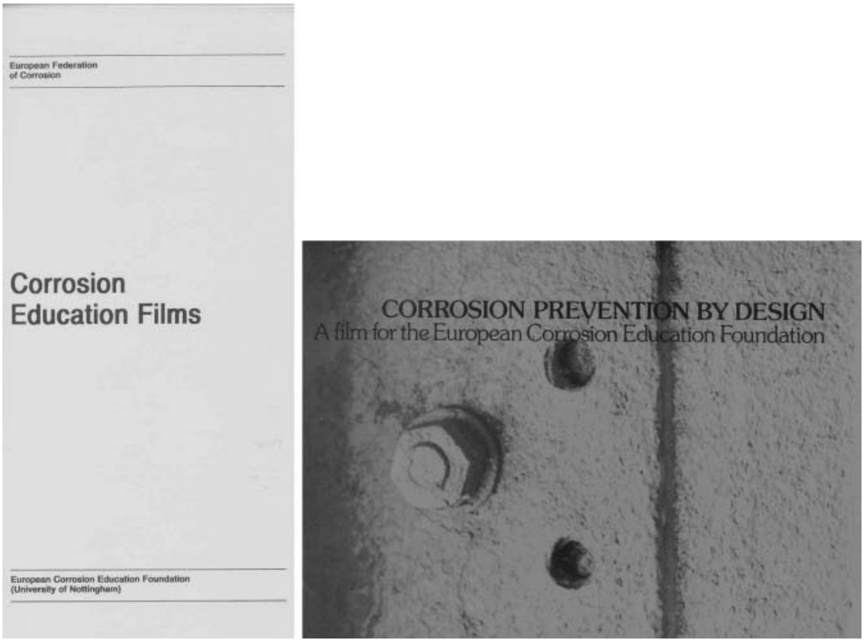
EFC

Published for
The European Federation
of Corrosion
by
The Institute
of Materials

5.4 *Corrosion Education Manual* published by the IoM costs increase considerably. However, if such materials are planned for a wider market, the cost can be brought down. This aspect was explored in the early discussions of WP7. Educational films on corrosion and corrosion prevention were intended to provide corrosion awareness to engineers, designers and others, in particular to those without detailed training in or experience of corrosion. The films are also of particular interest to management and to a wider audience, including student engineers and the general public. A Corrosion Film Committee was established under the chairmanship of Professor J. S. L. Leach (UK), and to carry out the administrative business it was established as a non-profit foundation, the European Corrosion Education Foundation, registered in the UK (Fig. 5.5). Three educational films on corrosion were produced by WP7 in conjunction with the Corrosion Education Foundation under the supervision of Professor Leach and Dr P. Boden (UK), namely, *Corrosion Prevention by Design*, *Corrosion Control by Protective Coating*, and *Corrosion Control by Changing Environment*. A film on materials selection was also planned. The films illustrate commonly found problems in industry and show practical solutions with enough theory to explain the principles upon which the corrosion process works. They also relate prevention to cost and maintenance. The original film versions are in English, but they are also available in French, German, Dutch, Italian and Swedish. Videotape versions of these films were also produced. All of these films provide factual information and make a particularly effective use of graphics to illustrate the concepts.

5.3.3 Books

Although the audio-visual media predominate at present, traditional methods of teaching were not forgotten. WP7 stressed the need for a textbook suitable for

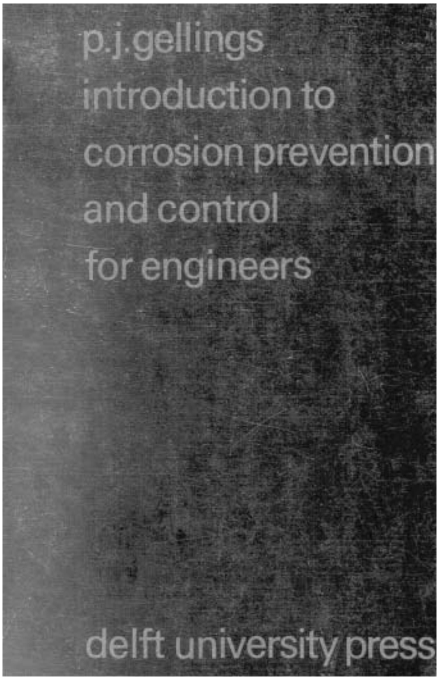


5.5 Sales catalogue of the EFC films and a leaflet of the film *Corrosion Prevention by Design* engineering schools. Professor P.J. Gellings (The Netherlands) took it upon himself to write the book, with the assistance of an editorial board nominated by WP7. Under the title *Introduction to Corrosion Prevention and Control for Engineers*, it was published in 1976 (Fig. 5.6). Several editions of this book have been published. A German version, *Korrosion und Korrosionsschultz von Metallen. Eine Einfürung*, is also available. This book gives an overview of what corrosion is, what its significance is, and how it can be controlled and prevented. The general methods used to prevent or control corrosion and their fields of applicability are discussed. Attention is given to the importance of design in preventing corrosion losses and to the economics of corrosion control.

A very effective and successful book is *Practical Corrosion Principles*, a collection of educational corrosion experiments produced by WP7 and published in 1989 (Fig. 5.7). The aim of this book was to illustrate the various types of corrosion phenomena and the methods used for their control. It contains details of corrosion experiments for use in the training of those with little previous specialist experience in the subject. It is intended for particular use in courses where corrosion protection is taught to engineers and scientists as an adjunct to their main area of work. At present, the book is out of print and a new improved edition is in preparation.

5.3.4 Courses

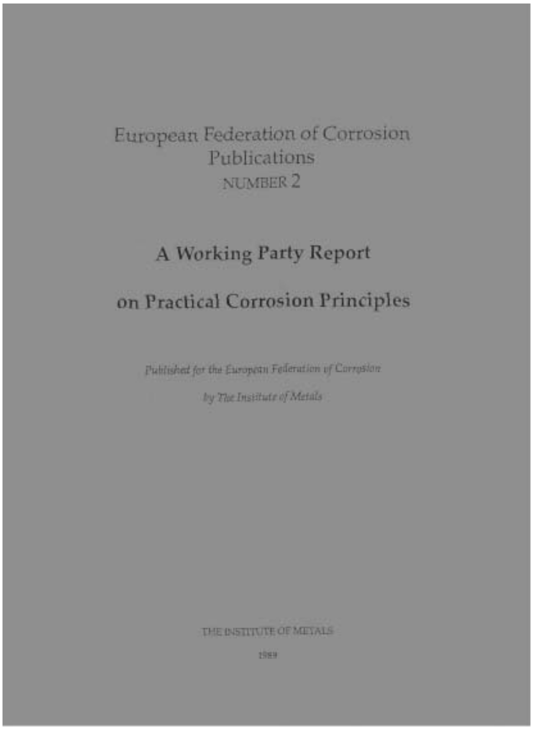
Even though WP7 has not been engaged in organising courses of its own, it participates in the organisation of courses in conjunction with other educational bodies or EFC working parties. The *International Summer School on Corrosion Inhibitors*,



p.j.gellings
introduction to
corrosion prevention
and control
for engineers

delft university press

5.6 The book of P. J. Gellings, *Introduction to Corrosion*



European Federation of Corrosion
Publications
NUMBER 2

A Working Party Report

on Practical Corrosion Principles

Published for the European Federation of Corrosion

by The Institute of Metals

THE INSTITUTE OF METALS

1989

5.7 Practical corrosion principles

organised by the Working Party on Corrosion Inhibitors in Ferrara, Italy, merits special mention here.

5.3.5 Survey of corrosion courses

The idea of collecting information on corrosion courses presented at universities and colleges emerged during a business session of WP7. Although WP7 itself has not developed any courses, a catalogue of established European corrosion courses is a valuable contribution. A questionnaire to collect details on teaching activities in the member countries, including degree courses, postgraduate courses, and post-experience courses, was prepared and distributed for completion by teachers from educational institutions engaged in corrosion, under the coordination of the WP7 member in their own countries. A preliminary report of the survey was carried out [4]. Detailed breakdowns of information are provided on course titles, course sources, academic levels of the courses, types of postgraduate courses, subject areas of degree-level courses, course duration, study regime, examination requirements, and time devoted to lectures, tutorials and practical work as a function of the type of course.

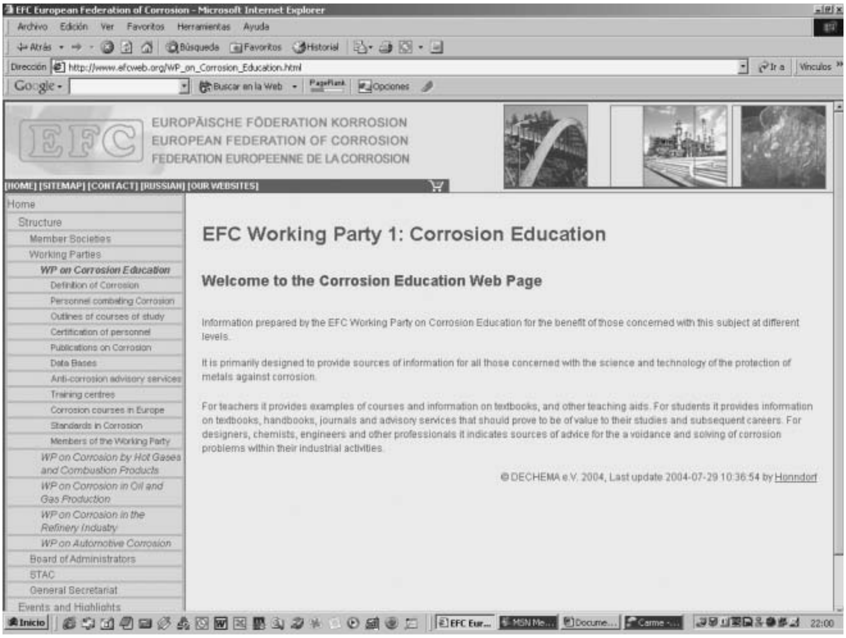
5.3.6 Participation in EUROCORR

As a consequence of active requests from a previous chairman, Professor D. Landolt (Switzerland), WP7 has played an active part in organising a session on corrosion education during EUROCORR meetings [5]. These sessions include papers authored by members of WP7. An idea that has received some attention in education sessions is the use of educational simulations; some mathematical simulations on computer are at present flourishing in corrosion education [6]. WP7 has been involved in a conference session on the occasion of EUROCORR conferences since 1995.

5.3.7 WP7 web pages

The explosive growth of the Internet in recent years has changed not only corrosion science but also corrosion education. Information being located on the web represents one of the most valuable advantages in promoting information exchange on the Internet. The EFC recently started a website, and WP7 was aware of the need for an educational page as a valuable tool for teachers and others looking for help with problems on corrosion education and to show where improvements in educational standards are needed.

In the role of adviser and informer to anyone interested in corrosion, WP7 is not as well known as it should be. To help overcome this deficiency, WP7 prepared an enlarged version of the *Manual on Corrosion Education* in electronic form, and it is available on the working party's web pages (see www.efcweb.org), as shown in Fig. 5.8. These pages provide sources of information for all those concerned with the science and technology of protection of materials against corrosion. They include definitions of corrosion, a classification for personnel combating corrosion, outlines of corrosion courses, certification of personnel, publications, databases, anti-corrosion advisory services, training centres, corrosion courses in Europe, standards on corrosion, and a list of WP7 members.



EFC Working Party 1: Corrosion Education

Welcome to the Corrosion Education Web Page

Information prepared by the EFC Working Party on Corrosion Education for the benefit of those concerned with this subject at different levels.

It is primarily designed to provide sources of information for all those concerned with the science and technology of the protection of metals against corrosion.

For teachers it provides examples of courses and information on textbooks, and other teaching aids. For students it provides information on textbooks, handbooks, journals and advisory services that should prove to be of value to their studies and subsequent careers. For designers, chemists, engineers and other professionals it indicates sources of advice for the a voidance and solving of corrosion problems within their industrial activities.

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5.8 Welcome to Working Party pages

5.4 Activities in progress

The activities just described represent the efforts of WP7 to address the trends initially noted. Present work is concentrated in the following areas.

5.4.1 Certification

Certification and qualification of corrosion experts is considered to be a very important activity. WP7 has been interested in certification since 1990. It was agreed to set up a sub-group, chaired by Professor G. Schmitt (Germany), to study new developments in the field and to make recommendations. The first job was to collect information on the systems of certification and qualification applicable to corrosion workers in the countries represented in WP7. A report from Professor Schmitt, presenting a picture of types of certification operative in Europe, was discussed during the meeting in 1991. Progress in the area of certification was reported in the meeting of 1992, including questions arising from the CEN initiatives. In 1993, it was agreed that an effective activity of WP7 would be to obtain and compare information on existing national and international schemes on certification. Information was gathered in 1994, and Professor Schmitt was requested to present a summary at the meeting of 1996. In its meeting of 1997, WP7 approved some actions in this way, paying attention to present and future legal requirements and restrictions on the ability of individuals to practise in corrosion technology, including both initial and continuing education and training. Various certification levels were proposed in the Schmitt report, as a function of the resposibility: (a) manual execution of corrosion control measure; (b) design, specification and monitoring of corrosion control measures; and (c) more highly qualified activities in corrosion and corrosion control than levels (a) and (b). WP7 does not intend to get involved in the actual certification of persons, but it might be asked to give advice on curricula and requirements. It is ready to develop work concerning certification in Europe, and, of course, to collaborate with other groups, e.g. in a task force, to establish criteria for certification of personnel and to harmonise planned certification systems [7,8]. Also, it was agreed that other relevant working parties, e.g. the Working Parties on Physicochemical Test Methods, Coatings and Cathodic Protection will be consulted.

5.4.2 MENTOR-C Project

The MENTOR-C Project was sponsored by the Leonardo Agency under Framework 6, with the EFC acting in a coordinating role. The project has now been completed, and discussions are ongoing about how best to exploit the products, which are distance learning course materials for vocational training in corrosion. They include digitised versions of the three EFC videos, in connection with which there will be some financial return to the EFC. WP7 also participated in a test evaluation of this project.

5.4.3 Computer-aided learning

The capabilities of personal computers have been increasing during recent decades, and this development will continue in the future. In order to provide support for corrosion education, cooperation with other bodies has intensified for the production of computer presentations on CD-ROM to help students learn the key concepts of corrosion science. Some projects are now underway.

5.4.4 Education–industry cooperation

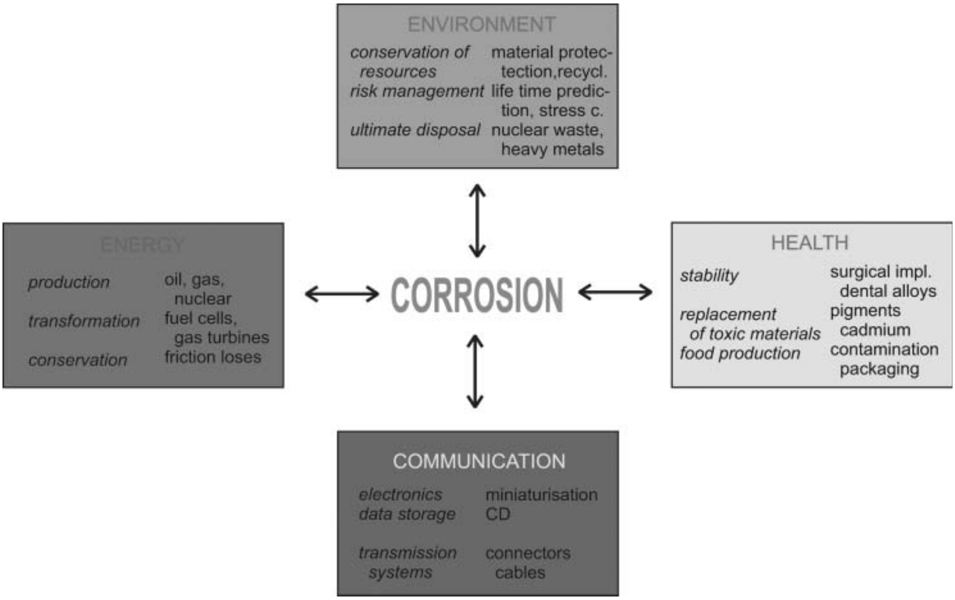
The need for better understanding and exchange of information and personnel between industry and educational institutions at all levels is widely accepted. Encouragement from industry and university should be given to realistic schemes for promoting education–industry cooperation at local, national and international levels.

5.5 Closing remarks

Faced with the challenges of the present millennium, WP7 is formulating its plans for dealing with major new activities concerning new teaching and learning approaches that will be effective without compromising quality.

The future of corrosion and therefore, to a great extent, also of corrosion education depends on creative adaptability regarding the challenges of corrosion. Corrosion is increasing in the volume of content, in the scope and level of the mathematical formulations of corrosion concepts, and in its diversification. On the other hand, the needs of humans, especially those concerning materials, which increase with the advance of civilisation, are related to materials stability, for which corrosion education offers much in terms of technology and application in everyday life. Figure 5.9 shows some impacts of corrosion in different socially relevant problems facing the community.

Europe and the rest of the world are in the midst of an educational evolution. Present changes as a consequence of the information revolution are likely to lead to



5.9 Impact of corrosion on the community a significant increase in demand for further education. This carries a need for life-long learning, which may involve distance learning, and maintaining and even improving its quality. In this way, information is a commodity that can be packaged, marketed and delivered to the home. Probably, the demand for life-long learning will increase significantly in the future.

The development of computer-based corrosion education packages that is currently underway, and also the use of computer-based conferencing to maintain contact with the distance learning students, will provide a comparable high-quality learning experience to that of traditional learning. The growth of E-mail, course websites, instant-messaging software and online courses has forced many teachers to rearrange their daily routines and has made them more accessible to students. The student interaction with teachers and other students is an essential characteristic of distance learning.

The new educational technologies will enable better tuition in corrosion and protection, leading to the popularisation of corrosion science and to an increased awareness of the hazards of corrosion. They constitute a promising tool that expands the learning horizons of students of all ages. This more profitable dissemination of information represents, of course, a crucial factor in determining the long-term future of corrosion education.

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6

Physico-chemical methods of corrosion testing

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6.1 Development of the field of measuring techniques in corrosion science and technology

The working field of Working Party 8 on Physico-Chemical Methods of Corrosion Testing (WP8) is extremely wide, since no publication or report on corrosion phenomena can do without reliable measurements. It is therefore neither possible nor desirable, considering the scope of this publication, to give a summary of the full development of the science and technology in the area. Moreover, it is closely related to the areas covered by some of the other working parties; thus, some overlap would exist. Nevertheless, some very important items will be mentioned. For a good overview of the field in direct relation to the activities of WP8 up to 1977–1978, we refer to two papers, by W. A. Schultze [1] and Parkins and Mercer [2].

Around 1980, the use of impedance spectroscopy gradually became fashionable in corrosion science. Although the technique was no longer really new, as a result of the fundamental work of Professor Sluyters at the University of Utrecht in The Netherlands in the two decades before, it was nevertheless some time before it could be used as a common tool, when good commercial equipment became available. The First European Corrosion Workshop on Impedance Measurements was organised by Professor de Wit from Delft University of Technology, as a separate session at EUROCORR '87 in Aachen. The event was timely and a great success, with 21 oral contributions from all over the world discussing the possibilities and problems in this fast-evolving field. The attendance of this workshop was such that it was necessary to move to a bigger lecture hall. After this, a regular series of independent so-called EIS conferences was established, which continues until today. The technique is now so well incorporated into our toolset that it has started to suffer from the normal over-maturity phenomena: important issues such as goodness of fit and over-complexity of models are not often well discussed anymore in papers. Nevertheless, the technique is a very valuable addition to the existing DC (Direct Current) techniques available, and is now also available for more localised measurements, which leads us to the second item: the local probe techniques. Since 1990, the scientific field of corrosion technology and electrochemistry has been experiencing a scientific revolution, due to the development of local probe techniques, which enable study of the relationships between microstructure and corrosion properties at the micrometre and sub-micrometre scale. While the historic development of corrosion science started with a simple deterministic and thermodynamic local approach to the phenomena observed, ironically the theoretical quantitative back-up of the phenomena only became possible after the development of the mixed potential theory, which included the kinetics, but did average out the current density over the full surface area of samples, rendering quantitative interpretation of real local phenomena such as pitting and galvanic corrosion virtually impossible. The local probe techniques do combine the best of both worlds: local information on the thermodynamic and kinetic data. They encompass a range of various techniques, the most important being: atomic force microscopy, scanning vibrating electrode technique, Kelvin probe, scanning Kelvin probe force microscopy (SKPFM), scanning reference electrode technique (SRET), scanning droplet cell (the microcapillary cell), and local electrochemical impedance spectroscopy (LEIS).

A third important development in techniques for measuring corrosion phenomena is the explosion in surface-sensitive analytical tools such as: scanning auger; X-ray photoelectron spectroscopy; ellipsometry; time of flight secondary ion mass spectrometry (TOFSIMS); glow discharge optical emission spectrometry (GDOES); environmental scanning electron microscopy; and high-resolution transmission electron microscopy (TEM). For high-resolution TEM, the preparation of samples has always been the most difficult part of the technique; the new possibilities given by the focused ion beam in preparing thin cross-sections through corrosion layers are very promising.

For studies of the interface between coatings and alloys, highly sensitive Fourier transform infrared reflection absorption spectroscopy should be mentioned, and for some applications, the contact electrical resistance technique.

Another promising group of techniques, especially for monitoring, comprises noise measurements. These techniques are, after a certain period of hype-fed expectations with ups and downs, now slowly taking their place in corrosion science.

Overviewing the developments in measuring techniques in the last 25 years, it is clear that exciting new possibilities have arisen, which have revived the whole field of corrosion science and will enable the experts to model corrosion phenomena much better, eventually leading to the design of sustainable system solutions based on durable materials.

6.2 The contribution of WP8

WP8 developed in the 1980s under the chairmanship of Dr L. Clerbois and Mr R. Grauer (Belgium), with the aim of studying the bases and application of physicochemical testing methods in the field of corrosion. From 1994, the chairman of WP8 was Professor Dr Hans de Wit, who was asked to devote the attention of WP8 to problems close to industrial interests, the transfer of existing and new methods, including the assessment of their reliability, being of great interest to industry.

From the following short description, it will become clear that the activities of WP8 closely reflect the changes in the field over the years as described above.

WP8 produced a report entitled *A Literature Review of Polarization Resistance B Values for the Measurement of Corrosion Rate*, which was published by NACE. It also produced a paper called ‘Scaling of corrosion tests’ for the ISE meeting in Erlangen in September 1983, and went on to consider corrosion testing in non-aqueous media. A workshop on ‘Electrochemical corrosion testing with special consideration of practical applications’ was held at the Corrosion Study Centre ‘Aldo Daccó’ of the University of Ferrara in September 1985. This included techniques for the measurement of potential, current and polarisation. The proceedings were published as a monograph in the DECHEMA Monograph Series. In 1990, it produced a report, *Guidelines on Electrochemical Corrosion Measurements*, for publication as No. 4 in the EFC Series. It went on to organise a round-robin exercise to compare the results obtained by several workers using different computer-assisted methods when studying the behaviour of one material in identical solutions.

Up to this point, only DC electrochemistry and no local techniques were involved in parallel with the developments in the field as described above. Since 1994, when Professor de Wit became chairman, WP8 has been engaged in close cooperation with other working parties, including WP6 on Surface Science and Mechanisms of Corrosion Protection, WP14 on Coatings, and WP17 on Automotive Corrosion, in the transfer of knowledge to industry by organising intense, well-attended sessions at the EUROCORR meetings.

WP8 has a clear policy on its attitude towards new measuring techniques. It has tried several times to organise a more focused session at the EUROCORR meetings, e.g. on electrochemical impedance spectroscopy (EIS) or SKPFM. In this way, a session mainly concerning EIS, devoted to the use and interpretation of impedance measurements for bare metals, was organised at EUROCORR '96 in Nice. It served its purpose: to transfer knowledge based on the experience of various scientists to (also) industrial colleagues. In a poster session, the other techniques were accommodated. At EUROCORR '99 in Aachen, the session dealt with a combination of EIS, SRET and noise measurements.

However, it became clear that real new techniques could not be discussed at too early a stage at the broad EUROCORR meetings. Thus, the impedance session in NICE was only successful because EIS had reached a certain level of maturity. Therefore, it was preferred to organise meetings on these novel topics by close cooperation with the other working parties at a time when enough scientists had experience with one or the other techniques. By that time, the technique had mostly found its first niche of applications, and it was much better to organise these events within that field of application. As a recent example, WP8 collaborated with WP6 to organise a workshop on 'Local probe techniques for corrosion research' during EUROCORR 2004 in Nice, and the proceedings have since been published as No. 45 in the EFC Series [3]. The cooperation with WP14 on coatings extends over many years, due to the extensive application of EIS in coatings research.

The reason for the existence of WP8 thereby became first to accommodate all high-level scientific contributions with a focus on measuring techniques for the EUROCORR meetings, and second to pre-select and follow-up new developments together with the other working parties. In this way, at every EUROCORR meeting, a good and, irrespective of the wide range of techniques available, well-attended meeting was organised over the years by WP8 while supporting other working parties with special topics.

A final activity aimed at transfer of knowledge to industry was the initiation by Professor de Wit of WP17 on Automotive Corrosion Phenomena at EUROCORR '98 in Utrecht, with which very close cooperation exists.

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7

The history of Working Party 9 on Marine Corrosion

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7.1 Introduction

For immersed structures in sea water, several types of corrosion can occur, depending on the material that is exposed. Over the years, several research areas have been covered, including: the characterisation of sea water, the establishment of test facilities, immersion testing, laboratory testing, electrochemical corrosion testing, modelling of corrosion mechanisms, and studies of interactions between biological activity and corrosion in sea water. Several corrosion mechanisms have been found to affect materials in sea water: uniform corrosion, bimetallic corrosion, pitting, crevice corrosion, erosion–corrosion/impingement attack, intergranular corrosion, selective corrosion, stress corrosion cracking (SCC), corrosion fatigue, and hydrogen embrittlement [1]. Some findings that were reported during the early days will be referred to below as an introduction to marine corrosion. In addition, some observations on the work of European Federation of Corrosion (EFC) Working Party 9 on Marine Corrosion (WP9) will be made.

The field of marine corrosion has a long history. Testing in sea water was in progress during the 1920s and 1930s. Over the years, the original research area has been developed, and new aspects have been added. In the first test programmes, tests were undertaken on Cu–Ni and Ni–Cu alloys as well as on stainless steels [2,3]. It should be noted that as long ago as 1824, cathodic protection was used on naval ships in order to protect the copper cladding from corrosion. Results from experiments with sacrificial anodes of zinc and iron were also reported in the early days [4].

A common situation in marine service is that two or more dissimilar metallic materials are connected electrically to each other and immersed in sea water. In this case, bimetallic corrosion can occur. One of the first examples of bimetallic corrosion was reported as early as in 1681, when lead sheeting and iron sheeting were put together [4].

It is known that mild steel corrodes with a uniform corrosion rate of 0.1–0.6 mm/year, and also that corrosion fatigue can take place in sea water [1]. It has also been shown over the years that several factors influence the corrosion rate of mild and low-alloy steels in sea water, i.e. fouling and microbiological effects such as those of sulphate-reducing bacteria. In order to protect these alloys, cathodic protection has been used. In 1943, Stuart and Evans reported that hydrogen evolution, as a consequence, for instance, of cathodic protection can decrease the fatigue life of structures and influence the lifetime of steels, but the use of zinc sacrificial anodes has a beneficial effect on the fatigue lifetime [5].

In the area of test methods, efforts were made to study corrosion resistance in marine atmospheres during the 1930s, and as early as 1939 the ASTM salt spray test, which is still used today [6], was standardised. In laboratory experiments, an important issue over the years has been which test solution should be used. Synthetic solutions with similar compositions of inorganic salts to those in sea water have often been used. As a substitute for natural sea water, synthetic sea water has been introduced, and in 1975 the ASTM published the first version of a standard for synthetic sea water containing all of the major constituents and some of the minor ones of natural sea water [7]. The use of ferric chloride for testing stainless steel is not new; recommendations for its use were made both in the USA and in Sweden during the late 1930s. However, the ferric chloride test was not standardised until 1976, when the original version of the ASTM G48 standard was issued [8].

For stainless steels, a large research area for the last 30 years has been the formation of a biofilm on stainless steels that causes ennoblement and hence a higher corrosion potential that increases the risk of pitting and crevice corrosion. According to [9], the first recording of this ennoblement was made as early as 1940, but no attempt to explain the observed phenomenon was made at that time. In 1976, studies in Italy and in 1983 in Norway found that the ennoblement is due to biological activity that affects the susceptibility to corrosion of stainless steels in sea water.

It should be noted that stainless steels are not the only materials that are able to form passive layers that have been used in sea water. Copper-based materials such as Cu–Ni alloys and brasses have been used in sea water for more than 60 years [10].

7.2 WP9 on Marine Corrosion

WP9 is more than 40 years old. It was established following an initiative by the French member societies of the EFC that was made after the International Congress of Marine Corrosion held Cannes in June 1964 [10].

The objectives of WP9 can be defined as follows:

- to provide engineers, designers and materials specialists with information related to the use of materials in the marine environment;
- to provide a forum for the discussion of materials-related aspects of marine corrosion by interested parties from industry and academic institutions;
- to identify and to define areas in which information is not up to date or not available in the required form;
- to identify areas in which research and development is required;
- to establish and maintain contacts with other workers in the same area and either cooperate with them or avoid duplication of activities.

In order to meet these objectives, the following actions have been taken:

- organisation and participation in workshops, seminars and conferences;
- preparation of guidelines on all aspects of marine corrosion;
- to either undertake research or stimulate others to do so in areas where a lack of scientific knowledge has been shown to exist.

In 1964, J. Talbot (France) was appointed as the first chairman of WP9. By 1974, the chairmanship had succeeded to Mr H. Arup (Denmark), and in his report to the EFC Science and Technology Advisory Committee that year, he reported that work on welds had started with a bibliography and that the selection of suitable test methods for an inter-laboratory test programme had begun [11]. The activities of WP9 decreased for a while, and no activities were reported in 1976 [12]. In a report on EFC activities during 1977 and 1978 [13], it was claimed that WP9 should be quickly revived, since the area was becoming more interesting, due to the discovery of North Sea oil and gas.

Mr D. B. Peplow (UK) was nominated as the new chairman of WP9 in April 1980. The activities of WP9 at that time included the preparation of a report in 1981 dealing with SCC of welded high-strength steels in marine environments in 1981. The compilation of information on corrosion in heat exchangers in ships, power plants and offshore platforms was undertaken at the same time [14]. In 1983, Mr Peplow resigned as chairman, at a time when WP9 had 16 members from 11 different countries. The work on SCC of welded high-strength steels had by then been impeded by a lack of financial support, but work on an atlas on failures had started, and was near to a first draft. It is reported that Hans Arup led the organisation by WP9 of a symposium on high-strength steel in sea water in December 1983 [15].

In 1985 [16], E. B. Shone reported on a joint meeting of the Danish Corrosion Centre and WP9 that had taken place on 29–30 November 1984, organised by H. Arup. This successful meeting covered corrosion problems in ships, power plants and offshore platforms. It was divided into sessions that dealt with pumps, valves, piping and heat exchangers, with a final session that dealt with complete systems. The additional requirements imposed on materials by the need to achieve weight savings were discussed, and it was shown that most materials used in sea water could fail prematurely in service because they were used beyond their limitations. At that time, there was limited experience with high-alloy stainless steels, and considerable interest was shown in the use of titanium [16].

During the 1980s, WP9 continued with the work on the atlas of marine corrosion failures and literature studies. In 1989, it was responsible for the third publication in the EFC Series, a working party report with the title *General Guidelines for Corrosion Testing of Materials for Marine Corrosion*. The author of the report was Professor F. P. Ijsseling, and it was reviewed by a group led by the chairman of WP9, Mr E. B. Shone, which included four of WP9's 13 members. The report is an extensive literature review on sea water as a test environment, and contains 24 pages with 143 references. It covers testing for ten different types of corrosion in marine environment, and materials ranging from mild steels to titanium as well as copper alloys and stainless steels are discussed [1].

Only 1 year after its first publication in the EFC Series, a second WP9 report was issued, concerning the work on the atlas of corrosion failures, with the title *Illustrated Case Histories of Marine Corrosion*. By this time, Professor Ijsseling had been elected chairman of WP9, and the report was assembled by a sub-committee that included himself, C. Christensen, R. O. Muller, J. G. Parker, E. B. Shone, J. Tavast and B. Todd. Failures of mild steel, galvanised steel, cast iron, Cu–Ni alloys, stainless steels, different types of brasses and titanium were included in this publication. The book includes 89 case histories divided into four groups: pipes, pumps, valves and heat exchangers. Each one provides information about the type of installation, the material used, the type of damage and the cause, remedial measures and comments [17]. All cases are illustrated with pictures that, together with an introduction about corrosion types and materials used in marine environments, made the report a valuable textbook for failure analysis. At that time, the membership of the EFC's working parties had been broadened [10], and this was reflected in the membership of WP9, which had increased to 20 members.

In the same year as the book of case histories was published, two events in which WP9 was active took place. The first was a deep water seminar organised by WP9 together with VERITEC near Bergen in Norway on 31 May and 1 June 1990. The chairman of WP9, Professor Ijsselling, chaired the workshop. Its ten presentations covered a wide area, including: testing, corrosion monitoring, cathodic protection and the corrosion behaviour of different materials in deep water such as High Strength Low Alloy (HSLA) steels, aluminium alloys and stainless steels [18]. The second was the 1st European Marine Corrosion Forum, which took place in Amsterdam on 25–26 September 1990. It was arranged as a series of informal discussion sessions with no written contributions or records. Discussions in the first session covered different issues relating to stainless steels: PREN; SCC; and ferric chloride tests of welds. The second session dealt with biofouling, chlorination, microbiological activity and cathodic protection. In the third session, sea water systems were discussed, including aspects such as the relative merits and life cycle costs of copper alloys, stainless steels and glass-reinforced plastic materials. The final session concerned atmospheric corrosion, coatings and computer systems [19].

In 1991, WP9 supported two events. The first was an international workshop on stainless steels and chlorination in sea water, and was organised in Brest on 29–30 May 1991 by IFREMER Centre de Brest. The second event was sponsored jointly with WP10 on Microbiologically Influenced Corrosion, and was an international symposium on marine and microbiological corrosion. It was organised by the Swedish Corrosion Institute, and was held in Stockholm from 30 September to 2 October 1991. Most of the papers from the event were published in 1993 as No. 10 in the EFC Series, *Marine Corrosion of Stainless Steels: Chlorination and Microbial Effects*. This publication was produced in collaboration together with WP10, and contains 17 contributions. Both conferences demonstrated the need to attack the marine corrosion problem in an interdisciplinary way [20].

In the late summer of 1992, WP9 collaborated with COIPM (Comité international permanent pour la recherche sur la préservation des matériaux en milieu marin) in the 8th International Congress on Marine Corrosion and Fouling, which took place at Taranto, Italy. The topics of the various sessions included microfouling, marine corrosion, fouling communities, microbiologically induced corrosion, fouling control systems, protective coatings and cathodic protection. It had 50 oral presentations with 20 posters and an attendance of 139 participants. The conclusion was similar to that after the event in Stockholm; an interdisciplinary approach was essential to make progress in the field [21].

An important activity in WP9 was initiated in 1992; a round robin test programme was set up in order to map the differences in sea water corrosivity of stainless steels at 11 test stations of European laboratories. The round robin comprised monitoring of the free corrosion potential and reduction current of UNS S31254 stainless steel in sea water, crevice corrosion testing of three stainless steel grades, UNS S31600, UNS N08904 and UNS S31254, a comparison of the critical pitting temperatures determined in sea water for UNS S31600, and monitoring of sea water parameters during the exposures. Two exposures were made, each of 6 months' duration, one during the winter and one during the summer. Potential ennoblement due to biofilm formation was registered at all test sites, but the results for initiation of crevice corrosion differed significantly between the test stations. The round robin was reported at a workshop that was organised by SINTEF Corrosion and Surface Technology in cooperation with both WP9 and WP10 in Trondheim in 1995.

Also in 1995, Mr B. Espelid succeeded as the chairman of WP9. In the following year, the publication of the proceedings from the workshop in Trondheim appeared as No. 19 in the EFC Series. This was a joint publication with WP10 with the title: *Sea Water Corrosion of Stainless Steels – Mechanisms and Experiences* [9]. As previously mentioned, it contained the results of the round robin test programme. During the first day of the Trondheim workshop, the topic was mechanisms of microbiological corrosion of stainless steel, including both the presentation of the round robin results and the closing seminar of the European Commission-funded project 'Marine Biofilms on Stainless Steels' in the Marine Science and Technology (MAST) programme. The MAST project had focused on the study of biofilm formation and crevice corrosion initiation on stainless steels. The outcome of the project was presented here, and increased our knowledge about the nature and mechanism of biofilm formation and its implications for stainless steels. On the second day, the workshop concentrated on industrial applications. The presentations concerned more highly alloyed stainless steels, some of which were very new at the time, as well as cathodic protection, pitting and crevice corrosion of stainless steels [22].

During 1994 and 1995, WP9 was looking into what standards, recommended practices, guidelines, etc. in the marine corrosion field existed in Europe [23,24]. At the same time, a review of marine corrosion test stations in Europe was undertaken. After the work with the standards, etc., it was recognised that there was a need to prepare guidelines for testing the susceptibility of stainless steels to localised corrosion in natural sea water. The aim of these guidelines was to contribute towards the improved reliability of test data on stainless steels in general, as well as to contribute to the safe use of these materials in marine environments. By 1996, the work on developing new guidelines had started with representatives of manufacturers and users of materials and representatives from testing laboratories [25].

In the following years, WP9 was involved with two literature surveys and also contributed to a European-funded project on crevice corrosion testing of stainless steels for use in sea water, which later became the CREVCORR project. One of the literature surveys had been started in 1993, and was focused on crevice corrosion in sea water. This study was made by Professor F. P. Ijsseling, initially with the support of Professor U. Steinsmo. The survey was eventually published in 2000 as No. 30 in the EFC Series. This contains 1082 references, and is a very useful reference book. It provides an overview, and although this concentrates on stainless steels, it covers many other alloys as well. There are three extensive chapters on 'Theory and modelling of mechanisms', 'Test methods' and 'Mechanisms conditions, applications and experimental results of specific alloys types'. In addition, two shorter chapters deal with 'Protection against crevice corrosion' and 'Crevice corrosion monitoring' [26]. The size of the chapters indicates that, during this period, extensive research was being undertaken on stainless steels in addition to that in WP9, which was discussed previously.

In 2001, WP9 published its next volume, No. 33 in the EFC Series, with the title Marine *Corrosion of Stainless Steels – Testing, Selection, Experience, Protection and Monitoring*. This was edited by Dr D. Féron, with a review committee that included J.-P. Audouard, B. Espelid, D. Féron, A. Mollica, E. Rislund, T. Rogne and B. Wallén. In Europe, two test programmes on crevice corrosion of stainless steels were performed in the 1990s, as discussed above, and presented, for instance, in the 1996 workshop in Trondheim, the papers from which were included in No. 19 in the EFC Series [9]. The first part of this includes five chapters concerned with the comparison of sea water corrosivities in Europe, among which, as an introduction, is the paper about the WP9 robin robin from EFC No. 19. Also in this part, three other chapters report further information, such as experimental details and critical temperature data from WP9's round robin test programme. The last chapter in the first part of the book compares the results of the EFC round robin with those from the exposures in the MAST project. The three other parts of the volume deal with: 'Material selection'; 'Testing and experiences'; and 'Monitoring'. In total, the publication contains 28 chapters [27].

The CREVCORR project, which was mentioned earlier, was initiated in WP9, and the then chairman, Mr B. Espelid, was the coordinator of the project, which was partly funded by the European Commission. During the project, WP9 acted as a reference group, and some members were active in the collaborative testing programme. The aim of the project was to develop a new test methodology for characterising the susceptibility of stainless steels to crevice corrosion in natural and treated sea waters. Experimental procedures to perform crevice corrosion testing were developed, including a spring-loaded crevice set-up and a new synthetic sea water with biological capacity that was capable of simulating the potential ennoblement due to the biofilm. Round robin test programmes were carried out with the new crevice formers, using both natural and the new synthetic sea water. The result of the project was that the crevice set-up that had been developed showed considerable improvement as compared to the earlier round robin test programme performed in Europe. Furthermore, good agreement was also found with the new synthetic sea water, indicating that it could be used to qualify stainless steels for sea water service. The new synthetic sea water has also been proposed for standardisation via ISO/TC 156 (Corrosion of Metals and Alloys). The project ended in 2003. Since the project had been initiated in WP9, a special workshop was held during EUROCORR 2003 in Budapest, in order to present the outcome from the project [28]. Furthermore, in order to describe the test methodology that had been developed, including the new synthetic sea water with biological capacity, it has been decided to prepare a new publication in the EFC Series [29].

The other literature survey, which was performed around the year 2000, was undertaken by Dr J. Birn, with the title *Corrosion of Copper and Aluminium Alloys in Sea Water*. The literature survey covered the period 1979–2001, and contained more than 400 references. Part 1, with more than 70 pages, includes chapters on: 'Theory and modelling of corrosion mechanisms of copper alloys in sea water', 'Effect of chlorine and other biocides of copper alloys in sea water', 'Aspects regarding brasses', 'Aspects regarding cupronickel alloys', 'Aspects regarding bronzes', 'Effects of pollutants on the corrosion of copper alloys in sea water', and 'Protection of copper alloys against corrosion in sea water'. Part 2 contains about 50 pages with similar chapters about aluminium alloys as for the copper alloys and aspects of Al–Mg alloys, Al–Mg–Zn alloys and Al–Li alloys [30]. A summary of this literature survey was the subject of the keynote lecture to the Marine Corrosion session at EUROCORR 2004 in Nice [31].

Also at EUROCORR 2004, a special workshop was held on copper and aluminium alloys in sea water, in addition to the usual session on marine corrosion [32]. The objective of this successful workshop was to cover the research on these alloys for sea water applications during recent years. It was organised by Mr B. Espelid, Dr D. Féron, Dr G. Ferrari and Dr M. Jassner. Among the topics included were overviews of copper and Cu–Ni alloys, testing, and experiences, including recommendations based on experience with the use of copper and Cu–Ni 90/10 alloys. Two of the ten presentations concerned aluminium alloys, including a keynote lecture by Professor K. Nişancioğlu with the title ‘Corrosion and protection of aluminium alloys in sea water’. With Dr D. Féron as editor, the organisers, together with Mr W. Schliech, served as the reviewing committee for publication of the proceedings of the workshop together with a few selected contributions made at earlier EUROCORR conferences. This publication, which makes an important contribution to the literature, contains 12 contributions distributed within the following sections: ‘Overview on copper and aluminium alloys’; ‘Copper alloys’; ‘Aluminium bronzes’; ‘Aluminium alloys’; ‘Aluminium-based anode materials’; and an overview of ISO standards relevant to the marine corrosion of these materials [33].

In 2004, Mr B. Espelid resigned as chairman of WP9, and Mr U. Kivisäkk (Sweden) was elected as his successor. At that time, WP9 had over 50 members on its mailing list. In addition to the activities mentioned above, WP9 has, during its history, organised marine corrosion sessions at EUROCORR, held one or two meetings per year to discuss technical issues, and been responsible for a session at the Marine Corrosion Forum [34].

7.3 Conclusion

WP9 has carried out numerous activities during the more than 40 years for which it has existed. Several projects have been carried out, including a round robin test programme of sea water testing. Furthermore, a project partly funded by the European Commission has been initiated by WP9. Several WP9 reports have been published over the years, and workshops and conferences have been organised or supported by WP9.

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8
Microbiologically influenced corrosion

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8.1 Introduction

Over the past 50 years or so, the involvement of microorganisms in the corrosion process and the consequences arising from it have received increasing interest and attention from scientists and engineers. During the early years, the development of knowledge, conceptual models and experimental techniques with which to understand microbiologically influenced corrosion (MIC) was rarely coordinated between disciplines. In fact, the differences in experimental techniques, terminology and application tended to hinder the effective transfer of knowledge and information. Therefore, in January 1987, the inaugural meeting of the new European Federation of Corrosion (EFC) Working Party 10 on Microbial Corrosion (WP10) took place in Trondheim, with the late Mr Kenneth Tiller (UK) as its chairman.

The 1st EFC Workshop on Microbial Corrosion was held with support from Professor C. A. C. Sequeira and the local societies at Sintra in Portugal on 7–9 March 1988. The workshop was the first attempt to bring together those in the European scientific community who are interested in this subject and to encourage an improved awareness of the problem. The proceedings of this first workshop were published in 1988 [1].

This was followed by a second workshop at Sesimbra, Portugal, in 1991, the proceedings of which were published as No. 8 in the EFC Series [2]. The workshop was held in order to follow up on the progress made since 1988. It covered: mechanisms, metallurgical factors, analysis, experimental control, case histories and non-metallic materials. Specific papers investigated basic electrochemical concepts, biosensors, voltammetry, microbial corrosion of stainless steel and copper, and new types of microbial corrosion, including biofilms and microbial biodeterioration of non-metallic material, notably in an architectural context. At that time, the first expert systems and databases had been developed for MIC, and the one presented in the proceedings should even today enable engineers to acquire rapid knowledge and understanding of MIC and provide advice on how to control and prevent it.

WP10 also arranged for an English translation of *Mikrobiologische Materialzerstorung und Materialschutz* (*Microbiological Degradation of Materials and Methods of Protection*), to appear as No. 10 in the EFC Series during 1992 [3]. It included two papers from WP10: 'Biofilm monitoring in sea water' by A. Mollica *et al.*, and 'Microbial and biochemical factors affecting the corrosion behaviour of stainless steels in sea water' by V. Scotto *et al.* These papers covered: aspects of marine corrosion and testing for sea water applications; experience with sea water chlorination on copper alloys and stainless steels; and an intelligent probe for *in situ* assessment of the susceptibility to hydrogen-induced cracking of steel for offshore platform joints.

Dominique Thierry (Sweden) then took over the chairmanship of WP10, and the 3rd Workshop on Microbial Corrosion was held in Estoril, Portugal, from 13 to 16 March 1994. The proceedings subsequently appeared as No. 15 in the EFC Series [4]. The purpose of this workshop was not only to follow up the progress made since 1991, but also to draw on experience from other countries. Experts from North and South America, Russia and Japan contributed to this workshop. During the workshop, it became increasingly clear that the need for an interdisciplinary approach to MIC is paramount for understanding its mechanisms and for developing mitigation strategies. Also, the workshop discussed biofilm sensors and their commercial use for the first time in Europe, some of them based on the electrochemical noise technique, which had been discussed during earlier workshops. Other topics included work on the microbial corrosion of copper at various centres in Europe, case studies with stainless steel, aluminium brass, carbon steels, etc., and topics such as groundwater engineering and fuel tanks.

Another book, No. 22 in the EFC Series, contained the proceedings of the session on microbial corrosion from EUROCORR ’96 [5]. The 11 chapters of this volume presented reports given in the MIC session at EUROCORR ’96, together with a paper from the working party on the economics of MIC in relation to power station performance. Much attention was given to the currently important subject of biofilms, particularly on stainless steel in sea water. There were descriptions of the characteristics of biofilms, and their effects. The volume concluded with an account of biological effects in power stations, the economic implications, and prevention methods.

The 4th Workshop on Microbial Corrosion took place in Lisbon on 6–9 June 1999, and the proceedings appeared as No. 29 in the EFC Series [6]. The papers in this volume covered: mechanisms of microbial corrosion, including stainless steel; biofilms, particularly the nature of those on copper surfaces, both in hospital water systems and in sea water; MIC of restorative dental materials; the effects of bacteria on cathodic protection; biofilm monitoring in cooling water systems and the use of organic biocides; case histories covering such diverse topics as the deterioration of archaeological stone and marble by lichens and algae, and biocorrosion in drinking water, in underground sulphur mines and in cooling water systems of petroleum refineries; and biodeterioration of sulphide ores and the bioleaching of Fe–Si alloys. This book contained several original papers that markedly improved our understanding of MIC, in particular the role of biofilms, and their chemistry, function and structure. The keynote paper reviewed and summarised microbiologically influenced corrosion in the context of microbe–metal interactions, with particular emphasis on selective electron transfer and the redox characteristics associated with the electrochemical reactions of the corrosion process.

At about the same time, WP10 began assembling a directory of European experts in MIC and helped to establish a European network on MIC (BRRT-CT98-5028). The purpose of this network was to bring together scientists and engineers from European industries, research organisations and universities to promote scientific and technological cooperation in order to improve the understanding of MIC phenomena, to assess its risk, and to propose effective ways for its mitigation. The multidisciplinary character of the project required the promotion of effective communication between all the different partners involved in the network. This was achieved in three ways:

1. By enhancing the relationships between academic teams with different backgrounds (biochemistry, microbiology, electrochemistry, and materials) in order to improve the fundamental understanding of microbiologically induced degradation and/or corrosion.
2. By encouraging exchanges between engineers from different industrial sectors, each of whom possessed specialist knowledge of MIC prevention in different application areas. This exchange of experience enabled the development of more efficient techniques.
3. By creating multiple links between academic teams and industrial research and development groups. This provided the academic investigators with access to new specific MIC cases and practical applications on an industrial scale. On the other hand, the connection with academic researchers helped the industrial partners to organise their own approach concerning fundamental well-identified topics and to define more efficient strategies against MIC.

In 2001, Rolf Gubner (Sweden) succeeded Dominique Thierry as chairman of WP10. Attention has since been focused on the organisation of strong sessions at EUROCORR. In the future, interfacial interactions between materials and the living environment will be one direction of scientific research and exchanges within WP10.

8.2 Introduction to MIC

Microbiologically influenced corrosion, sometimes referred to as biocorrosion, is the deterioration of metal through corrosion processes that occur, directly or indirectly, as a result of the metabolic activity of microorganisms [7]. Bacteria, for example, have a size of about 1 μm, and 1 mL of water might contain about 10^{12} cells, providing an active surface area of about 1 m^2. Microorganisms influence corrosion processes by several mechanisms that operate simultaneously or consecutively. Only rarely does a single cause account for microbial effects on corrosion [8]. Owing to the complex nature of MIC, research into this field demands both an understanding of microbial effects and a knowledge of corrosion science [9]. The process of MIC occurs most frequently when a metal is immersed in an aqueous phase containing microorganisms that adhere to its surface. The attached cells are capable of growing, reproducing and forming a biofilm. The latter is an assemblage of microorganisms and their extracellular polymeric substances (EPSs), such as carbohydrates, proteins, nucleic acids and lipids [10]. The biofilm may trap scale, rust and other inorganic matter as well as organic detritus composed of dead cells and metabolites. The resulting layer can greatly influence the corrosion reactions taking part at the metal surface. The presence of a biofilm can create physical anomalies on a metal surface, resulting in the formation of local anodic and cathodic regions [11]. Non-uniform colonisation of the surface might lead to the formation of differential aeration cells [12]. A single type of microorganism can simultaneously affect electrochemical processes via several mechanisms, such as metal oxidation or reduction, organic and inorganic acid production, the release of enzymes, hydrogen production or the secretion of EPSs [13]. In reality, biofilms are composed of microbial communities that may facilitate electrochemical processes that individual species cannot [14]. Synergistic activities within mixed bacterial cultures can lead to an increase in the corrosion rate [15,16]. Research by Dickenson *et al.* [17,18] has suggested that biogenically formed manganese dioxide might act as an electron acceptor in the cathodic reaction of the electrochemical corrosion cell, hence causing depolarisation of the cathode. The product, MnOOH, might be biogenically reduced to the original compound, MnO_2 [19].

The acronym MIC is frequently used for 'microbially influenced corrosion', and refers to the possibility that microorganisms are involved in the deterioration of metallic (as well as non-metallic) materials. MIC is not a new corrosion mechanism, but integrates the role of microorganisms in corrosion processes. Thus, an inherently abiotic process can be influenced by biological effects. A suitable definition of MIC, which has been developed in the European Network on MIC (BRRT-CT98-5028), is the following:

> Microbially Influenced Corrrosion (MIC) refers to the influence of microorganisms on the kinetics of corrosion processes of metals, caused by microorganisms adhering to the interfaces (usually called 'biofilms'). A prerequisite for MIC is the presence of microorganisms. If the corrosion is influenced by their activity, further requirements are: (I) an energy source, (II) a carbon source, (III) an electron donor, (IV) an electron acceptor and (V) water.

The role of MIC is often ignored if an abiotic mechanism can be invoked to explain the observed corrosion. MIC, as a significant phenomenon, has thus been viewed with scepticism, particularly among engineers and chemists with little appreciation of the behaviour of microorganisms. The slow progress in establishing the importance of MIC in equipment damage is also the result of the paucity of analytical techniques to identify, localise and control corrosion reactions on metal surfaces with surface-associated microbial processes. In the meantime, MIC has become increasingly acknowledged during the last decade in books [20–24]. In some cases, MIC has become the 'joker' where there is no plausible electrochemical explanation for a given corrosion case. In order to better understand under which conditions MIC is possible, some basic questions will be answered here. Microorganisms are commonly subdivided into fungi, algae, diatoms and bacteria.

8.3 Microorganisms involved in MIC

Fungi typically metabolise hydrocarbons and, when associated with corrosion, are filamentous and yeast-like, branching and weaving themselves into a tangled mass. This is a source of differential aeration cells, which can then lead to pitting and often to localised attack, which may be accelerated due to the secretion of metabolic products such as organic acids [25]. An example of corrosion due to fungal activity is the damage to aircraft fuel tanks caused by *Hormoconis resinae* (formerly *Cladisporium resinae*). This organism survives on a nutrient mixture of water, fuel and dissolved oxygen at the water–fuel interface. As a metabolic product, *H. resinae* secretes organic acids that lower the pH and can cause severe pitting of aluminium [26].

Algae and diatoms are chlorophyll-containing organisms found in sea water and fresh water. Their role in corrosion is thought to be similar to that of fungi [27].

The final class, bacteria, is composed of unicellular organisms. Their role in the deterioration of metals is wide-ranging and depends upon the species. Numerous studies have reported cases of MIC of steel in marine habitats [28]. The role of sulphate-reducing bacteria (SRB) is unequivocally accepted [29]. However, the possible mechanisms by which SRB initiate or enhance corrosion processes are subjects of continuing discussion.

Aerobic bacteria are prevalent in all aquatic environments, where their primary role in corrosion appears to be in colonising the surfaces, creating oxygen-depleted microenvironments in which anaerobic bacterial species, e.g. SRB, can grow, initiating differential aeration cells and excreting corrosive acids [12,30,31]. The accelerated corrosion of stainless steel in sea water by aerobic *Pseudomonas* spp. and their exopolymers has been demonstrated [32]. Facultative anaerobes, such as the marine *Vibrio* species, have been reported to enhance the adhesion of SRB to steel surfaces, thus increasing metal corrosion [33–35]. It has been demonstrated that the presence of the aerobic *Oceanospirellum* and associated EPSs can lead to the development of localised anodic areas. Corrosion rates in mixed cultures have been found to be greater than in pure cultures, and synergistic effects have been observed. An example is provided by metal-depositing bacteria, which may require the presence of other bacteria such as SRB. Types of bacteria that are commonly associated with the MIC problem are listed below:

- SRB, e.g. *Desulfovibrio* spp. Several textbooks have been published about SRB and their role in corrosion, e.g. Postgate [36] and Barton [37]. SRB belong to the class of obligate anaerobic bacteria.
- Sulphur-oxidising bacteria (SOB), e.g. *Thiobacillus ferroxidans* [38], belong to the group of aerobic bacteria, and have a wide distribution. It has been suggested that SOB grow in symbiosis with SRB [39], since both SOB and SRB are part of the natural sulphur cycle.
- Iron- and manganese-oxidising bacteria, e.g. *Gallionella ferruginea* [40].
- Iron-reducing bacteria, e.g. *Pseudomonas* spp. [41].
- Methanogenic bacteria, e.g. *Methanococcus thermolithrophicus* [42].
- Organic acid-secreting bacteria, e.g. *Escherichia coli* and *Serratia marcescens* [43].

8.4 Mechanisms of MIC

Several mechanisms of MIC have been proposed. They depend on the bacterial species as well as the environmental conditions, and can be classified as described below.

8.4.1 MIC due to bacterial metabolites

SRB reduce oxidised sulphur compounds, such as sulphate, sulphite and thiosulphate, as well as sulphur, to hydrogen sulphide (H_2S). The high content of sulphate in sea water favours the growth of SRB [44]. Although SRB are strictly anaerobic, it can be shown that some genera tolerate oxygen and are even able to grow at low oxygen concentrations [45]. Hydrogen sulphide is a weak acid and reacts with metal ions to form insoluble or weakly soluble sulphides. This can lead to high corrosion rates [46,47]. The sulphides generated on the metal surface can act cathodically on the metal, and hence increase the corrosion [48]. A study by Edyvean *et al.* [49] described a further effect of SRB and their metabolites on the corrosion process, due to hydrogen entry into and the growth of cracks in steels. A recent review on the role of SRB in anaerobic corrosion has been provided by Videla *et al.* [50].

8.4.2 MIC due to inorganic acid production

Microbially produced inorganic acids are nitric acid (HNO_3), sulphurous acid (H_2SO_3), nitrous acid (HNO_2) and carbonic acid (H_2CO_3). H_2S acts as a nutrient source for SOB, which then produce sulphuric acid (H_2SO_4) [51,52]. Sulphurous acid and sulphuric acid are mainly secreted by bacteria of the genus *Thiobacillus* [53]. Other bacteria, such as *Thiothrix* and *Beggiatoa* spp., as well as some fungi (e.g. *Aureobasidum pullulans*), also produce these acids. Thiobacilli are extremely acid-tolerant and can grow at a pH value of 1. Nitric acid and nitrous acid are mainly produced by bacteria belonging to the groups of ammonia- and nitrite-oxidising bacteria. The main problem in sulphuric and nitric acid corrosion is the fact that the resulting salts are water-soluble and, hence, the formation of a protective corrosion product layer is not possible. Furthermore, because of the lowering of the pH, protective deposits formed on the surface, e.g. calcium carbonate, can dissolve.

The third type of inorganic acid, carbonic acid, is produced by many life-forms. Carbonic acid, especially if present in high concentrations, can react with calcium hydroxide and form insoluble calcium carbonate ($CaCO_3$) and water-soluble calcium hydrogen carbonate $Ca(HCO_3)_2$. The latter is called aggressive carbonic acid.

8.4.3 MIC caused by organic acid production

Nearly all microorganisms secrete, while growing or throughout their lifetimes, organic acids [54–56], such as acetic, lactic or formic acid. Their role in biodeterioration is similar to that of inorganic acids.

8.4.4 MIC due to enzymatic activity

Organic materials, such as coatings, might be degraded by microorganisms due to the excretion of degrading exoenzymes [57] (depolymerases), which break the polymeric material into small and water-soluble fractions. These small fractions are often utilised by bacteria as a carbon source. Reports have been published discussing the microbial deterioration of coatings and the resulting corrosion attack [54,58,59].

Another example is hydrogen removal by the enzyme hydrogenase present in some species of SRB in an anaerobic environment [60]. Thus, the corrosion reaction would be indirectly accelerated by depolarisation of the cathode through the removal of atomic hydrogen from cathodic areas on the steel surface. This reaction will be coupled to the reduction of sulphate to sulphide, and the resulting corrosion products will be ferrous sulphide and ferrous hydroxide [61].

8.4.5 MIC due to manganese dioxide deposition

Stainless steels owe their overall corrosion resistance to the formation of a stable oxide film on the surface. Ennoblement of stainless steels is the increase of the free corrosion potential of a passive metal surface with the danger of inducing a corrosion reaction. Research by Dickenson *et al.* suggests that biogenically formed manganese dioxide might act as an electron acceptor in the cathodic reaction of the electrochemical corrosion cell, hence causing depolarisation of the cathode. The product, MnOOH, might be biogenically reduced to the original compound, MnO_2 [62,63]. This mechanism represents another clear demonstration of biologically induced/influenced redox reactions leading to a change in the electrochemical redox reactions of metal corrosion.

8.5 The role of biofilms in corrosion

MIC occurs in the presence of a biofilm. The latter forms immediately when a metallic surface is immersed in water. This is a process known as 'biofouling' [64]. Microbial cells exist in one of three states: planktonic, sessile or fragmental. Planktonic cells persist in bulk fluids and are free to move with the flow of this bulk fluid or even against it, if they have filaments. Sessile cells are those attached to surfaces within the biofilm, and most bacteria occur in this form in natural environments. The third state, fragmental, is a subset of the previous two, whereby sessile bacteria within the biofilm become detached with part of the biofilm and are dispersed within the bulk liquid. Although the cells are still in the biofilm, they are no longer attached to the substratum and are hence not truly sessile.

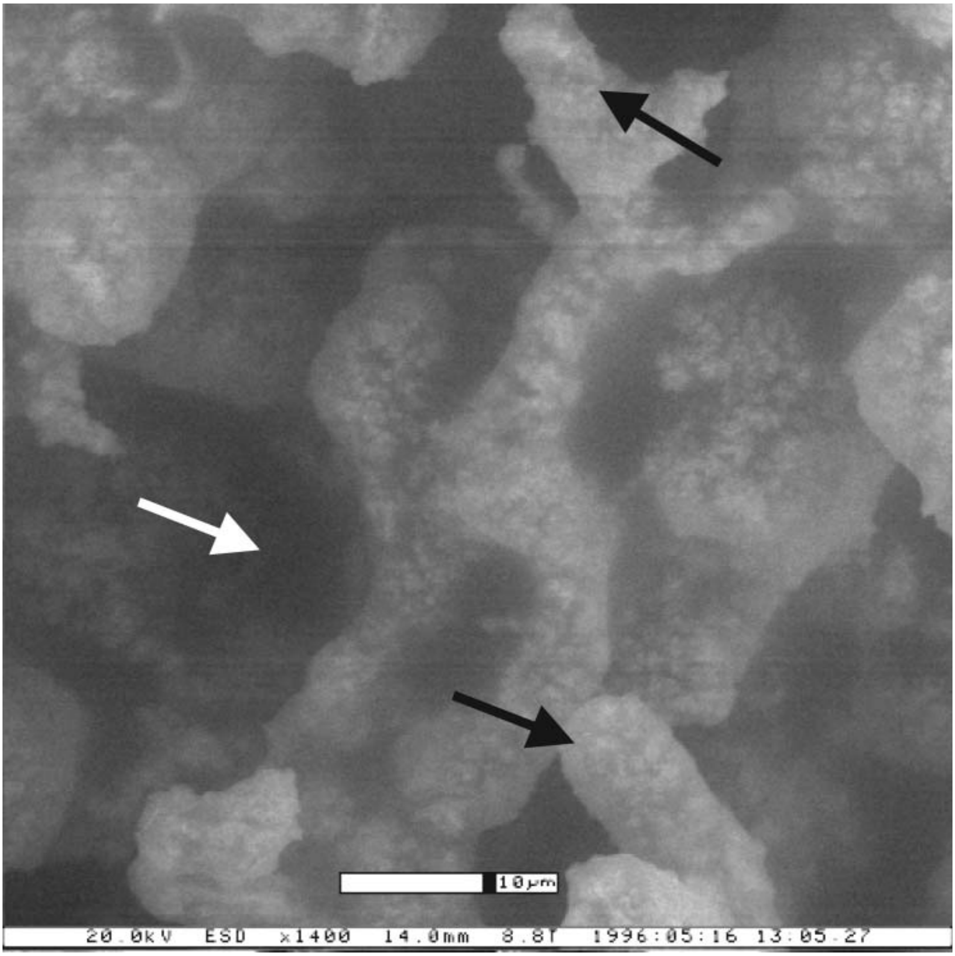
If bacteria colonise a surface, they often produce EPSs [65,66] to attach to a surface [67], grow, reproduce and synthesise more EPSs. This EPS layer gives the cells protection against drying out [68], toxic compounds (e.g. biocides or heavy metals [69,70]), shearing forces, and natural enemies (e.g. protozoa). Work by Beech *et al.* [71,72] has shown that EPSs produced by SRB are capable of binding large amounts of heavy metals such as iron and chromium. Furthermore, recent research revealed the direct involvement of EPSs produced by these bacteria in the deterioration of carbon steel [73]. These findings support earlier reports demonstrating the corrosive properties of EPSs [11,74].

The biofouling layer on the metal surface consists of immobilised microbial cells and colonies embedded in a matrix of EPSs that is adsorptive and porous. This organic matrix is capable of entrapping large amounts of material. Hence, biofilms are often found to be composed not only of microbial cells, EPSs and other bacterial waste products, but also solutes, heavy metals, corrosion products and inorganic particulate matter. Furthermore, it has been suggested that the formation of complexes due to microbial metabolic products might lead to the dissolution of otherwise insoluble inorganic matter, such as corrosion products, and hence to the removal of a protective layer.

8.5.1 Biofilm formation

The development of biofilms occurs in several stages. First, organic molecules in the bulk liquid are transported to the metal surface (substratum) and are absorbed onto the wetted surface, forming a conditioning film. The second stage is the attachment phase, whereby planktonic bacteria in the bulk liquid are transported to the substrate and a fraction of these attach for a finite period of time, before detaching. This process is known as reversible absorption. The detachment of these bacterial cells can be due to several factors, such as the flow rate and fluid shear forces. However, some cells do not become detached, and once they have been 'in residence' on the substratum for longer than a critical period of time, they become irreversibly attached to the surface. These irreversibly attached bacteria grow and reproduce at the expense of the substrate and bulk fluid materials. Hence, the biofilm grows and accumulates. At this stage, there is considerable production of EPSs, to the extent that a mature biofilm may only contain 10% dry weight in the form of bacterial cells. The final stage is the subsequent detachment of parts, or the whole, of the biofilm and its entrainment in the bulk fluid [75]. The current biofilm model was introduced by Costerton [76] and Lewandowski *et al.* [77]. Figure 8.1 shows an example of the heterogeneous biofilm structure.

The Costerton–Lewandowski model was based on observations made with confocal scanning laser microscopy together with oxygen microelectrode measurements. Oxygen concentration profiles within a metabolically active biofilm were correlated with biofilm structure under flow conditions. These measurements revealed that the cell clusters can vary in shape, ranging from cylinders to filaments, and that the clusters are attached to the substratum, forming 'mushroom' structures. In turn, voids (or pores) can penetrate the biofilm, reaching the substratum (Fig. 8.1).



8.1 Scanning electronmicrograph of a fully hydrated biofilm on a carbon steel test specimen exposed at Camber Dock, Portsmouth, UK, over a period of 13 months. Bacterial stacks can be seen rising from the surface (black arrows). The biofilm contains pores or voids (white arrow)

Within the biofilm, there will be a wide variety of microbial organisms, ranging from aerobic through facultative bacteria to anaerobic bacteria. These bacteria act symbiotically to produce conditions more favourable for the growth of each species [39,78]. For instance, obligate anaerobes such as SRB may not be thought to exist in the (oxygenated) environment. However, in reality, within the biofilm, aerobes would act effectively to remove oxygen from the immediate vicinity of the anaerobe. Of course, fungi, algae and diatoms are also present within natural biofilms, and have their role in the community. Biofilms also produce protective environments for microorganisms and, in most cases, allow different types of organisms to flourish that would not normally do so in the bulk phase. It is important to realise that of all the bacteria present in sea water, it is possible to grow less than 1% in the laboratory [79].

8.5.2 Biofilm and substratum interactions

It has been discovered that properties of the surface that the biofilm attaches to, the substratum, play an important role in microbial adhesion. It has been demonstrated that the composition of a metal substratum influences the formation rate and cell distribution of micro-fouling films in sea water during the first few hours of exposure [80]. In addition, electrolytic concentration, pH [81] and inorganic ions influence the settlement of the microbes [82]. It has also been found that passive metal films, either oxide or hydroxide, will form sites for the firm attachment of bacteria [83]. Some studies have demonstrated that microbial colonisation of a metal substrate appears to increase with increasing surface roughness [84–86]. Other researchers emphasise the role of surface energy [87] and hydrophobicity [88] in the adhesion process.

Biofilms can modify the environment at the metal surface by providing a physical and chemical barrier to the diffusion of chemical species such as oxygen [89], and by generating new chemical species, e.g. H_2S, that would not otherwise be present in the environment.

Biofilms are widespread throughout aqueous systems. The presence of biofilms does not necessarily lead to the formation of a corrosive environment. In fact, a number of workers have confirmed the protective nature of some biofilms [90], and biofouling is generally regarded as being beneficial for steel structures, e.g. steel sheet piling [39].

8.6 Conclusion

In principle, corrosion is an interfacial process. The kinetics of corrosion are determined by the physico-chemical environment at the interface, i.e. by the concentration of oxygen, salts, pH value, redox potential and conductivity. All these parameters can be influenced by microorganisms growing at interfaces. This mode of growth is preferred by most microorganisms on earth. The organisms can attach to surfaces, embed themselves in slime, so-called EPSs, and form layers that are called ‘biofilms’. These can be very thin (monolayers), but can reach a thickness of several centimetres, as is the case in microbial mats. Biofilms are characterised by strong heterogeneity. It is well known that the metabolic activity of clusters of biofilm organisms can change the pH value by more than three units locally. This means that, directly at the interface, where the corrosion process is actually taking place, the pH value can differ significantly from that in the water phase. Thus, water sample values do not reflect such effects.

In conclusion, MIC is not a ‘new’ corrosion process but is caused by the effect of microorganisms on the corrosion process kinetics. This can be very considerable; however, it is important to make sure that microorganisms are in fact involved in the process. This is necessary because MIC has become a kind of ‘joker’, explaining all kinds of otherwise unexplained corrosion cases. Therefore, it is important to consider under which conditions the participation of microorganisms is possible.

WP10 has contributed significantly to the current understanding of MIC worldwide and will continue to do so. Today, MIC is commonly accepted, and researchers from different disciplines have found a common language. Microbiologists and corrosion engineers now understand each other, thanks to workshops and MIC sessions held at the EUROCORR conferences. The role of extracellular enzymes in MIC is a hot topic for the near future. Progress in experimental design and analytical techniques allows researchers today to study interfacial phenomena at a level of detail that was impossible when WP10 started in 1987.

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9

Report on the work of EFC Working Party 11 on Corrosion in Concrete

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The first examples of major damage to concrete buildings induced by the corrosion of reinforcement were reported in the 1960s. Since about 1975, the amount of damage has increased considerably, causing the corrosion of reinforcement to become one of the major problems in maintaining the infrastructure. Most critical are structures exposed to chloride environments, such as offshore or coastal structures exposed to sea water (e.g. Fig 9.1) or bridges or parking garages exposed to de-icing salts (Fig. 9.2).

In addition, carbonation of the concrete can lead to depassivation of the steel and subsequent corrosion of the reinforcement, especially when the concrete cover is too low (Fig. 9.3) or in cases of insufficient compaction of the concrete (Fig. 9.4).

In aggressive environments, corrosion rates can be 1 mm per year or more. Figure 9.5 shows a rebar that has been partially corroded in the vivinity of a crack in a hot, salty environment within 4 years. In more moderate climates, the corrosion rates are usually lower, but they are still critical: Fig. 9.6 shows a rebar from a parking garage in Germany that was removed from the vicinity of a wide crack, where de-icing salts had gained access for about 10 years. The loss of cross-section has proceeded so far that the remaining load-bearing capacity of the steel is negligible.

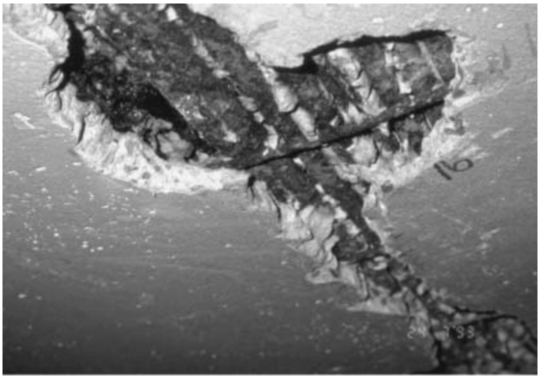
Following the realisation that corrosion of the reinforcement in concrete structures was a serious problem worldwide in the 1960s and 1970s, and that the amount of damage was still increasing considerably in the 1980s, extensive research programmes were initiated to investigate the mechanisms of reinforcement corrosion and to devise appropriate ways of assessing, repairing and maintaining the affected structures. Reinforced concrete probes with cable connections to each rebar have been used extensively to study the potentials, polarisation behaviour, macrocell effects and influences of the concrete mix, as well as the environmental conditions, such as temperature, humidity and chloride content (Fig. 9.7).

As such research was being carried out in many different countries, there was an evident need to exchange information about the increasing knowledge in this field. Consequently, a new European Federation of Corrosion (EFC) working party was formed in 1987, Working Party 11 on Corrosion in Concrete (WP11). Dr Bernd Isecke was its first chairman. Its initial activities included the preparation of reports on reference cells for use in concrete structures and on electrochemical rehabilitation

9.1 Example of chloride-induced reinforcement corrosion in concrete exposed to sea water

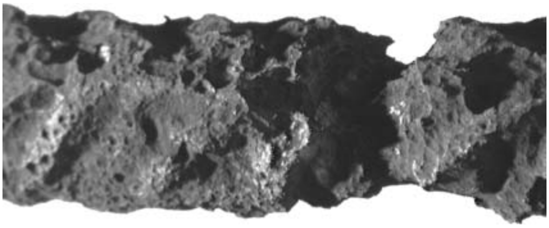
9.2 Example of chloride-induced corrosion of reinforcement exposed to de-icing salts within a leaking joint of a parking garage

9.3 Corrosion of the reinforcement of an old concrete structure caused by insufficient concrete cover



9.4 Corrosion of the reinforcement caused by bad local compaction of the concrete

9.5 Corroded rebar from a 4 year old building in a hot, salty environment



9.6 Corroded rebar from cracked concrete of a parking structure exposed to de-icing salts

9.7 Example of electrochemical testing of rebar corrosion in a concrete specimen

techniques. This eventually resulted in the publication of No. 24 in the EFC Series (see later).

In 1992, Professor Chris C. Page (UK) took over as chairman of WP11, and new sub-groups were formed to study coated and corrosion-resistant rebars, as well as the design of durable reinforced concrete structures.

In 1996, Dr Jürgen Mietz from BAM (Germany) became the new chairman of WP11. In the same year, WP11 became involved in COST 521, a collaborative European programme on the corrosion of steel in reinforced concrete structures. Furthermore, WP11 became involved in RILEM TC 154, working on methods for the measurement of corrosion in concrete.

An important topic for WP11 during that period was the development of electrochemical rehabilitation methods such as:

- cathodic protection
- electrochemical chloride extraction (desalination)
- electrochemical re-alkalisation of concrete

In particular, several different anode systems were developed for the cathodic protection of reinforcement, and these were discussed in detail in WP11. As examples, Fig. 9.8 shows the thermal spraying of a zinc layer onto the concrete surface to act as a sacrificial anode, and Fig. 9.9 shows the installation of a carbon mesh into a special conducting mortar for an impressed current cathodic protection system.

The successful application of these methods requires special knowledge of civil engineering as well as corrosion engineering. Within WP11, experts from both fields worked together to discuss the possibilities and limitations of these methods and details of how to improve their effectiveness. The results of this successful work were published in 1998 as the No. 24 in the EFC Series, entitled *Electrochemical Rehabilitation Methods for Reinforced Concrete Structures – a State of the Art Report*.

At about the same time, several excellent presentations were given at the EUROCORR 1997 conference in the session organised by WP11. Selected papers from this session were published in 1998 as No. 25 in the EFC Series, edited by J. Mietz, B. Elsener and R. Polder, and entitled *Corrosion of Reinforcement in Concrete: Monitoring, Prevention and Rehabilitation*.

9.8 Sacrificial cathodic protection of steel in concrete by thermal zinc spraying

9.9 Cathodic protection by impressed current using a carbon mesh anode in a special mortar

During the years that followed, major topics of WP11 continued to be general corrosion mechanisms and possibilities for corrosion protection. In 2000, No. 31 in the EFC Series was published, with the title *Corrosion of Reinforcement in Concrete: Corrosion Mechanisms and Corrosion Protection*, edited by J. Mietz, R. Polder and B. Elsener.

Another major topic of WP11 has been corrosion inhibitors for reinforced concrete. Different types of products developed during that period included the so-called mixed-in and surface-applied inhibitors. Tests showed that the corrosion rate could be reduced significantly under certain conditions. Extensive discussions have taken place in WP11 on the effectiveness, protection mechanism (pore blocking, passivation, chloride binding, etc.), fields of application (leaching-out effects, cracks, etc.), and durability of the different types of inhibitor. As a result of these discussions, No. 35 in the EFC Series was published by Task Group 2 of WP11 in 2001 (Table 9.1).

A special problem for reinforced concrete structures is the possibility of hydrogen-induced stress corrosion cracking of certain types of pre-stressed steel. This is an extraordinarily dangerous type of corrosion, because it can lead to the sudden failure of pre-stressed concrete beams or slabs without any prior warning such as evidence of corrosion or deflections or deformations of the structural element. Single collapses of pre-stressed concrete structures have clearly been identified as the consequence of such a hydrogen-induced corrosion mechanism. In 2003, No. 37 in the EFC Series was published by Task Group 4. This was entitled *Test Methods for Assessing the Susceptibility of Prestressing Steels to Hydrogen Induced Stress Corrosion Cracking*.

Two other EFC books were prepared under the chairmanship of Dr Juergen Mietz: *Corrosion of Reinforcement in Concrete: Mechanisms, Monitoring, Inhibitors and Rehabilitation Techniques* (EFC No. 38) and *The Electrochemistry and Characteristics of Embeddable Reference Electrodes for Concrete* (EFC No. 43). The latter book describes the results of Task Group 5 on ‘Reference Electrodes in Concrete’ (Table 9.1).

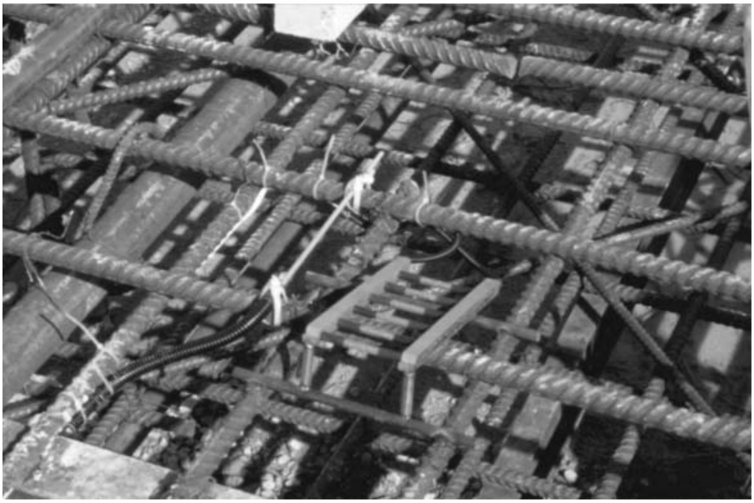
In 2005, Professor Dr Michael Raupach from the Institute for Building Materials Research at the Technical University of Aachen, Germany, took over as chairman of WP11. He has organised the sessions on corrosion in concrete of EUROCORR 2004 in Nice, EUROCORR 2005 in Lisbon, EUROCORR 2006 in Maastricht and EUROCORR 2007 in Freiburg.

Annual meetings of WP11 are traditionally held in conjunction with the EUROCORR conferences, and usually attract about 25 participants.

Professor Michael Raupach is continuing his work as chairman of Task Group 6 on Corrosion Models, where numerical models for the propagation stage of reinforcement corrosion are under discussion. Several researchers from six countries are contributing to this work, where numerical simulations of special case studies have been carried out and are being considered as the basis for a future service life design model. Valuable input data for this work are available from corrosion monitoring systems in actual structures (Fig. 9.10) and exposure tests.

Table 9.1 Task groups of WP11

Task group	Title	Chairman	EFC book
TG1	Electrochemical Rehabilitation Methods for Reinforced Concrete Structures	Mietz	No. 24
TG2	Corrosion Inhibitors for Steel in Concrete	Elsener	No. 35
TG3	Requirements of Concrete Cover Depth in Environmental Conditions	Gjorv	–
TG 4	Test Methods for Assessing the Susceptibility of Pre-stressing Steels to Hydrogen-Induced Stressed Corrosion Cracking	Isecke	No. 37
TG5	The Electrochemistry and Characteristics of Embeddable Reference Electrodes for Concrete	Myrdal	No. 43
TG6	Models for the Corrosion of Steel in Concrete	Raupach	–



9.10 Sensors installed in a concrete structure to monitor the corrosion risk for the reinforcement

As examples of exposure testing, Fig. 9.11 shows a measuring unit for exposure tests in the splash water zone of a highway in Germany, and Fig. 9.12 illustrates the exposure of concrete specimens in a sea water environment on the island of Helgoland. An extensive German research project on 'Corrosion Models for the Propagation Phase of Reinforcement Corrosion' will continue this work (www.bam.de/dfg537.htm).

9.11 Measuring unit of exposure tests within the splash water zone of a highway in Germany

9.12 Exposure tests in seawater on the island of Helgoland as part of a research project supervised by the University of Stuttgart

In addition to the work of these task groups, new activities are planned by WP11 in the fields of corrosion monitoring by Dr Ulrich Schneck, and new anodes for cathodic protection by Dr Bernd Isecke.

As a joint event together with WP4 on Nuclear Corrosion, WP11 participated in the NUCPERF 2006 international conference in Cadarache. During this conference, special attention was paid to the long-term durability of reinforced concrete structures with service lives much greater than the 50 years usually anticipated for buildings.

Now, WP11 is participating in the COST 534 project on the 'Protection of Pre-stressed Concrete' and is intending to participate in a new RILEM TC on Modelling of Reinforcement Corrosion.

Finally, it should be noted as a considerable success of WP11 that during recent years, sessions devoted to the corrosion of steel in concrete have taken place over two full days at every EUROCORR conference, showing the continuing interest in the work of WP11.

10

Corrosion in oil and gas production

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The European Federation of Corrosion (EFC) had traditionally arranged its activities by focusing on working parties with a common interest in a corrosion phenomenon such as stress corrosion cracking or cathodic protection. A successful working party had been established for some years on 'Corrosion in the Nuclear Industry', i.e. an industry-centred working party, when the idea for a European 'talking shop' for the oil and gas industry was suggested.

A driving force for starting this group was Don Harrop from BP, who played an active role in the EFC. Supported particularly by Jean-Louis Crolet, he approached the Nickel Institute for support in funding a chairman for the group and secretarial support.

The first meeting of Working Party 13 on Corrosion in Oil and Gas Production (WP13) was in 1993, chaired by Liane Smith. About 40 persons attended from across the industry, with support from the UK, The Netherlands, Norway, France and Italy. Over the following years, membership of the group grew rapidly, reaching a mailing list of about 180 within 2 years, with attendance at meetings (initially three per year, reducing to two after a few years) of about 50–60 persons. Membership grew to include representatives from the majority of European operators; engineering contractors; research organisations and consultancies. Attendees have included several Middle East operators and some from the USA, giving WP13 legitimacy as a key contributor to this truly international industry.

There was a strong drive to make a good contribution to the industry across national boundaries, and without the legalistic constraint of working on Euronorms. The EFC has maintained a strong reputation for good publications, driven by the excellent technical editors Tony Mercer and Paul McIntyre.

WP13 made a strong impact on that reputation by producing two key 'guideline' documents on H_2S cracking within about 18 months. These were EFC No. 16, *Guidelines on Materials Requirements for Carbon and Low Alloy Steels for* H_2S*-Containing Environments in Oil and Gas Production*, and EFC No. 17, *Corrosion Resistant Alloys for Oil and Gas Production: Guidance on General Requirements and Test Methods for* H_2S *Service*. Both publications remain in print, and have proven to be robust in their technical advice, having only undergone one editorial revision each within about 10 years. A new ISO standard, ISO 15156 1-3, has been developed on the issue of 'H_2S cracking of steels and CRAs'. The two EFC documents, together with NACE MR0175, formed the basis for this standard, which frequently refers to the EFC documents.

Publications have continued, with a classic volume on various aspects of CO_2 corrosion, No. 23, *CO_2 Corrosion Control in Oil and Gas Production – Design Considerations*. The latest publication, No. 39, *The Use of Corrosion Inhibitors in Oil and Gas Production*, was published in 2004.

The structure of WP13 was set up around working groups, each chaired voluntarily by members on a rotating basis. That structure has survived as a good model to this day. The meetings focus on key industry topics, changing with the technical challenges as they arise. Opportunities are given to hear about industry-driven research projects and to discuss, in a more leisurely way than is possible at conferences, interesting problems of data interpretation and failure analysis.

In 1998, the chairmanship of the group was handed over to Phil Jackman for 3 years, and it then passed to Stein Olsen, who was recently succeeded by Thierry Chevrot (France).

11

Corrosion control by coatings

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11.1 Introduction

Being older than the European Federation of Corrosion (EFC), I can remember when it was established. At that time, I was just asking the person who became my first boss, Professor Trabanelli, his advice about becoming a chemist. Then, as time went by, I remember that when I was about 50 years old, just as the EFC is now, I was full of hopes and wishes, convinced that many more things had to happen in the future. I wish all members and member societies of the EFC to feel the same, and that it might be true for the century.

By the way, we are used to considering that during the 20th century, an incredible amount of innovation, evolution and improvement was achieved. It is not deniable that, amid so many troubles, from 1914 to 1989, the everyday life of Western civilization became quite different as compared to the *belle époque*. But it is also true and well known that most of the innovation took off during the previous century: cars, aeroplanes, telephones, photography, microstructure and even nanostructure, today so popular, belong to the romantic times. The 20th century is characterised by the massive exploitation of what was handed over by the industrial and social revolutions of the 19th century, with a few exceptions: semiconductors, atomic energy, antibiotics, and polymers are among the main examples. Because of the need to handle enormous amounts of material, it so happened that the rate of turnover of objects, competition and finally globalisation inceased the need for suitable means and rules aimed at extending, or at least controlling, the service life of the myriad of objects, facilities and infrastructures that became available.

Hence the development of the science and technology of materials corrosion (first of all metals), almost totally ignored in past centuries, because of the elitist, careful use of the then scarcely available (and expensive) industrial, or better artisan, products. Corrosion science had a slow and difficult path, mainly due to the widely shared concept of the infinite availability of both resources and energy. It was only after World War II that the need for a more 'Scrooge-like' turnover was first evident, and Uhlig was allowed to demand of the UNO a strong effort to enhance both the knowledge and awareness of the problem.

It is now true and evident that the first aim was achieved, since most of the mechanisms of corrosion are now clear and the most sensitive and reliable test procedures have been established. Unfortunately, the second one is far from being achieved. The cost of corrosion, estimation after estimation, always remains inside the 3–4% of gross national product of an industrial nation. Actually, a recently published report

[1] showed that the direct cost of corrosion in the USA was approximately $275.7 billion per year, which is 3.1% of the gross domestic product (GDP). The industrial areas with major corrosion issues are the transportation and utilities industries, manufacturing industry, and federal, state and local governments. This percentage lies in the range that previous studies for various countries showed in the past.

However, the current study was more detailed, and specified corrosion costs using two methods: (a) cost of corrosion control methods and services; and (b) corrosion costs in individual industrial sectors. It is estimated that the indirect cost to the end user can double the economic impact, making the cost of corrosion, including indirect costs, $551.4 billion or more. This means that the overall cost to society could be as much as 6% of GDP. Often, the indirect costs are ignored because only the direct costs are paid by the owner/operator.

Of the available corrosion control methods, paints and corrosion control coatings make up the largest portion. Other commonly used methods include the use of corrosion-resistant metals and alloys, the application of cathodic and anodic protection, the use of corrosion inhibitors, and the use of polymers. The cost of corrosion-related services was estimated to be small.

The preventive strategies include the following:

- to increase awareness of large corrosion costs and potential savings;
- to change the misconception that nothing can be done about corrosion;
- to change policies, regulations, standards, and management practices to increase corrosion cost-savings through sound corrosion management;
- to improve education and training of staff with regard to corrosion control;
- to advance design practices for better corrosion management;
- to advance life prediction and performance assessment methods;
- to advance corrosion technology through research, development, and implementation.

Mainly on the basis of these statements, and it is noteworthy that basic research and development (R&D) is put as the last point, I consider still relevant and up to date the statement I proposed during EUROCORR ’97 in Trondheim, which was widely accepted and has also been reproduced [2]:

> I am far from saying that fundamental corrosion research is obsolete; but a corrosion scientist today is asked to remember that corrosion is a practical problem, an economic waste. Unfortunately, too many of those people who actually deal with critical operations related to durability and reliability, consider corrosion control a cultural and technical nonsense: they just ignore it and hence don’t care.
>
> A corrosion scientist, involved in his sacred and inviolable researches aimed to approach the . . . virtual world, should remember that by solving many practical everyday problems an innovation, an advancement of science, a good publication may come; in the meantime, it is coherent with the priority needs of our field of interest that are, between others: – education, continuing education at all levels of people involved; this is the most important item, since it is necessary to spread out knowledge of the very simple corrosion principles in order to avoid the most elementary mistakes!

Actually, there has been for long time, and still exists, a deep gap between corrosion science and corrosion control. Another, consequent, gap is between corrosion control technology and the widespread awareness of its practice. An exhaustive example of this fact is given by coating technology (the largest contribution to corrosion costs).

11.2 R&D in coatings

The use of a protective coating is the most immediate answer to the problem of protecting buildings, steel masts, offshore structures, bridges, chemical plants, vehicles, white goods, and also art. This is the simplest way to offer protection, at least conceptually: by separating the object from the environment. Today, the environment is, at least in many locations, less aggressive to our buildings and artefacts; at the same time, our sensitivity and perception of the danger is greater.

Apart from any aesthetic considerations, the use of protective coatings is today the object of great scientific and commercial interest, first because of growing demand for total quality, high performance and long useful life, and second because of the need to limit costs, to facilitate application, and above all to respect the environment.

It is also universally recognised that appropriate use of a coating or of a surface treatment can allow the use of more economical basic materials with good structural properties but little environmental resistance.

We must also note that a protective coating is not something that is simple or easy to create; many coatings are multilayer composites made up of a metallic layer (zinc, aluminium or alloy), a chemical pre-treatment (phosphatising, bonding primers, etc.), and a set of organic layers (primer, intermediate, enamel), each characterised by specific functions and properties. Moreover, today, many components are toxic or hazardous (chromium, lead, organic solvents, cadmium, etc.) and no longer acceptable, even though the alternatives often cannot offer the same performance.

In this context, the Industrial Anticorrosion Laboratory at Trento University has worked, since its inception (1980), on the properties of innovative coatings that are less toxic and polluting, but ever more resistant to electrochemical and mechanical degradation. In the last 10 years, the main interest of the laboratory has focused on composite coatings reinforced with micro-particles or nano-particles conferring special properties and/or having specific functions [3–8].

In this field, international research is very active, ranging from design and production of photo-catalytic surfaces to those resistant to degradation caused by environmental interaction. By environmental degradation, I mean not only the action of all gaseous and liquid corrosives present, but also impact by solid particles or contact with other adhering or moving surfaces (erosion, impingement, cavitation, and fretting), and the action of static and dynamic stress and strain (corrosion due to tension and fatigue).

In addition, under the coated surface, there must also be a ‘mass’ with adequate mechanical properties, that is easily worked and assembled and above all of low cost; an adequate surface treatment or coating must therefore be responsible for delaying degradation of the chemical, physical, mechanical and, not least, aesthetic properties of the item; in other words, of corrosion and wear.

From the above concepts, I wish to raise some further considerations, showing the peculiarity of coating technology (science and technology might be more appropriate, but in such a case one should involve metallurgy, polymer science, electrochemistry and more, of which coatings are a branch).

Whereas, in many branches of science and technology, progress has been achieved through new and better materials and methods (metals, polymers, composites, electronic, mecatronics, etc.), in corrosion control (and mainly by coatings) the evolution has been mainly driven by ecological and health restrictions. Actually, many extremely cheap and efficient surface treatments that have been available for a long time are strictly forbidden nowadays. Let us review the main examples.

11.3 Lead and chromium

In Italy, the majority of the bridges and viaducts are built of reinforced concrete. However, all over the world (and mainly in the USA), steel structures are mostly used.

According to the above-cited report, the total number of highway bridges in the USA is approximately 600 000, of which half were built between 1950 and 1994. The construction materials are concrete, steel, timber, masonry, timber–steel–concrete combinations, and aluminium.

Overall, approximately 15% of all bridges are structurally deficient, with the primary cause being deterioration due to corrosion. The mechanism is one of chloride-induced corrosion of the steel members, with the chlorides coming from de-icing salts and marine exposure.

There are approximately 200 000 steel bridge structures in the USA. Until the mid-1970s to late 1970s, virtually all steel bridges were protected from corrosion by three to five thin coats of lead- and chromate-containing alkyd paints applied directly over mill scale on the formed steel. Maintenance painting for prevention of corrosion of the majority of these bridges has been rare, and has been limited to larger bridge structures and toll bridges. Since the majority of the steel bridges in the interstate system were constructed between 1950 and 1980, most of these structures were originally painted in this manner. Therefore, a large percentage of the interstate steel bridges are protected from corrosion by an old coating system that is now beyond its useful life. Moreover, this coating system is considered to be hazardous to humans and the environment.

Actually, as a major side effect, with many social, economic and technical consequences, the safe removal of old toxic paints took years of trials and inactivity, leading to some disasters: some bridges, devoid of maintenance for so long, collapsed, claiming victims.

The consequent environmental regulations, which were established in the last 20 years, covered all aspects of steel structure painting, from construction to rehabilitation and routine maintenance.

The current maintenance burden for corrosion protection of steel bridges presents a major challenge to bridge owners. The past two decades have seen significant increases in the costs associated with steel bridge maintenance painting. As recently as 20 years ago, bridge painting was a relatively simple operation, with little emphasis on regulatory compliance, quality, or life cycle performance of materials. Bridges were either painted over repeatedly in a low-technology, low-cost attempt to combat corrosion and deteriorating aesthetics, or they were cleaned by open abrasive blasting and were repainted. Over the past few years, environmental regulations have become the single most influential force in the bridge painting industry, increasing the cost per square metre of steel from an average of $15 to more than ten times this price.

Specifically, regulations having a significant impact are those regarding:

- the volatile organic compound (VOC) content of protective coatings;
- environmental and worker health and safety associated with the removal of lead-containing paint.

Table 11.1 [1] lists the most pertinent regulations and summarizes their effect on bridge painting operations. It is noteworthy that a side effect of the environmental protection was the great improvement in scaffolding technology, in order to avoid

Table 11.1 Effect of regulations on coating operations

IMPACTING REGULATION	EFFECT ON COATING OPERATIONS
OSHA; CFR 29 1926.62, Lead in Construction, 1993	Establishes guidelines for protection and monitoring of workers removing lead paint from bridges. Requires lead training and monitoring for workers.
EPA; Resource Conservation and Recovery Act (RCRA), 1976	Regulates the handling, storage, and disposal of lead- (and other heavy metal) containing waste. Can increase the cost of disposal of waste from bridge paint removal by a factor of 10.
EPA; Title X, Residential Lead-Based Paint Reduction Act of 1992	Mandates training and supervision requirements for workers associated with lead-containing paint removal.
EPA; Comprehensive Environmental Response Compensation and Liability Act (CERCLA 1980 and Superfund 1986)	Assigns ownership of and responsibility for hazardous waste to the generator "into perpetuity."
EPA; Clean Water Act, 1972	Regulates discharge of materials into waterways.
EPA; Clean Air Act Amendments, 1070	Mandates restrictions on allowable VOC content of paints and coatings. Regulates discharge of dust into air from bridge painting operations.

interference of the work with the surroundings, and in grit- and water-blasting procedures.

11.4 Corrosion inhibitors

Now that those miracle protectors, principally red lead and chromates, are no longer available, the path towards efficient primers that really work is still long and uncertain. The most popular substitute, zinc phosphate in its many over-emphasised trade brands, is on its way to being excluded from the market because of restrictions concerning P_2O_5 release. A recent paper [9] from people who are among the highest specialists in corrosion inhibitors stated:

> Several years ago heavy metal based corrosion inhibitors were widely accepted as materials that could provide the corrosion protection needed. Corrosion inhibitors provide an indispensable function to protective coatings. The performance of a coating under corrosive environmental conditions requires that corrosion inhibitors provide sustainable protection during the warranty period of the coating. The coating industry however is challenged to be more cognizant of the impact toxic metals have on human health and the environment. In response to the European Directive 1999/45/EC Advancement of Technical Progress (ATP) amendment 29, effective October 2005, products containing zinc oxide and zinc phosphate require hazardous labelling due to their marine toxicity. The growing demand to replace zinc, barium, strontium and other heavy metals has shifted the coatings pendulum to more friendly [often] higher cost alternatives.

And yet one must point out that the protection offered by these outlawed products was very effective. This author remembers having seen a mains water pipe in a forest in Venezuela, painted with red lead alkyd in the time of Ymenez, and still rustless, as well as enormous ballast tanks of oil tankers primed with zinc chromate pigmented epoxies and finished with what today are equally forbidden coal-tar epoxies lasting for years and years of heavy duty service.

In the days of old, at the time of the first and second SEIC (symposia on corrosion inhibitors), the town of Ferrara was invaded by many Stetson hats, wide belts, and wire ties: Texan oil drillers were then looking for inhibitors that were active in acidic media, and there are still concerns about their use. On the other hand, the technology for metal pre-treatment and finishing was fulfilled: chromate as a primer, chromates as passivating agents. Those prototypes, archetypes of singular, total efficiency, were so satisfactory that the mechanisms of inhibition were not even completely investigated. Only after their 'apartheid' were some deeper studies started, but these were only aimed at the transfer of knowledge to possible candidate substitutes. In my laboratory, extensive studies on ion-exchange inhibitors were carried out [10] as well as on zinc-rich primers [11].

Owing to the same restrictions as were mentioned before, a long-used process that was the subject of extensive research culminating in a top-quality, high-efficiency method is approaching obsolescence: phosphatising plus chromatising.

The pre-treatment of metal surfaces before painting is an extremely delicate and critical process, often being responsible for the long-term reliability of a protective coating. Phosphatising is still widely used, but its days are numbered; and yet, the history of this process is full of successful steps: from hopeitic zinc phosphate [12], replaced by phosphophillite when cathodic Electrophoretically Deposited Paint (EDP) was introduced [13], and then by tri-cationic phosphate, to the phosphatising of zinc, of aluminium, and of their alloys [14]. The need to develop protective systems with reduced impact on both human health and ecosystems drove research to new products for metal surface pre-treatment, suitable for inducing adhesion of the subsequent paints. The classic chromatising, so widely used on both aluminium and galvanised steel, is increasingly being replaced by advanced chrome-free treatments (with some exotic diversions towards biocorrosion [15], with attempts to use the skeletons of bacteria as base pre-treatment of steel) based on zirconium and titanium salt-containing baths for both zinc and aluminium [16–19], which, together with a specific cleaning process [20], are also able to protect against filiform corrosion. An alternative path includes chromium III pre-treatment [21] and innovative processes making use of sol-gel technology [22]. A further quickly developing field is the use of silanes as adhesion promoters, with the important advantage of being applicable to items composed of different metals or alloys [23].

11.5 VOCs

The restrictions in VOC emissions greatly affected both the paint industry and the application of paints. Of course, any ecological act is welcome, even if the priority in its application is not always understandable: industrial emissions, transportation and house heating are much more harmful fields than coatings. As a consequence, it took about 10 years of attempts before water-borne paints approached the quality of solvent-borne ones, with many costly failures in practical applications.

I would like to present here an interesting table (Table 11.2), even if it is outdated, showing the situation with regard to estimated sources of photochemically reactive VOCs as seen by a paint expert (C. Velt, TNO Report 1992) in the period when switching from solvent- to water-borne paints was in full fashion. On this basis, it can be estimated that around 10% of European VOC emissions have come from coatings.

Table 11.2 Estimated sources of photochemically reactive VOCs

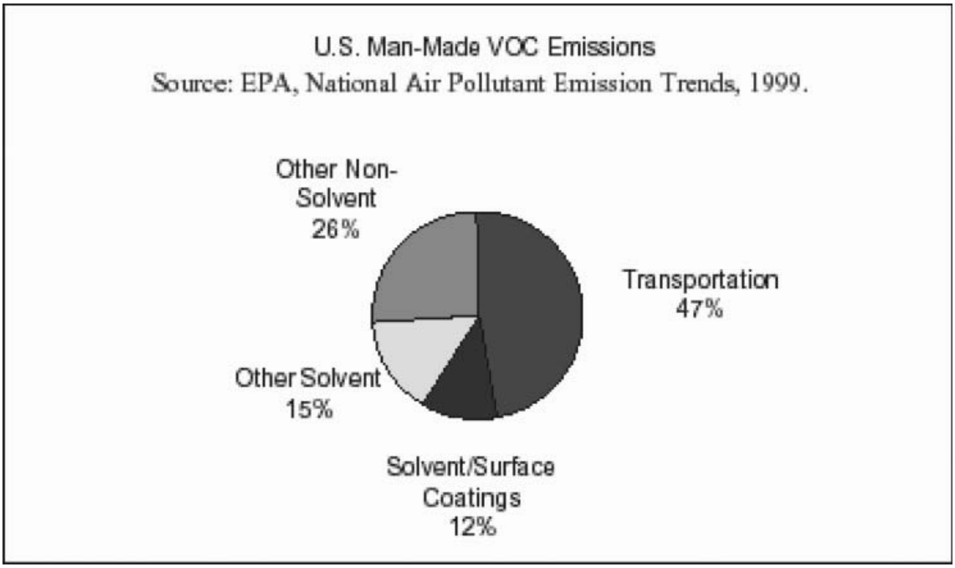
	Globally (%)	European (%)
Transport	9	35
Solvent use	5	20
Refinery and chemical processes	4	16
Stationary combustion sources	2	6
Natural emissions (e.g. terpenes)	80	23
Total	100	100

Of this percentage, industrial coatings account for roughly one-half, or 5% of the total emission.

Figure 11.1 shows that, in 1999, the situation was not much improved.

11.6 Metallic coatings

I will not deal in this paper with one of the most widespread and effective technologies, which greatly improved both the durability and aesthetics of steel structures: zinc coating. In its various methods of application (hot-dip, including Zn–Al alloys, electro-galvanising, hot-spray and coil coating), it has helped to extend the service life of millions of square metres of steel. Nevertheless, zinc, a heavy metal, is also under scrutiny for possible toxicity. Many other outstanding metal coatings have been totally abandoned or are under strict control before becoming obsolescent. The first was cadmium. Its replacement involved years of research, with an acceptable performance eventually being found in Zn–Ni alloy. The next was, obviously, chromium. Chromium is the perfect technical solution when a hard, smooth,



11.1 US man-made VOC emissions. Source: EPA, *National Air Pollutant Emission Trends*, 1999.

wear-resistant coating is demanded. It is also bright and elegant and, once a previous nickel coating is provided, corrosion of the substrate is easily avoided despite the micro-cracks that are always present in chromium plating. It is therefore clear how difficult it is to replace materials, and how hard it is to convince the industry to accept restrictions. There are many approaches to the problem, ranging from high velocity oxy-fuel (HVOF) coatings to nano-composite coatings, involving SiC nano-particles in an electro-deposited nickel layer [4–8]. Nickel itself has caused many problems, and is under scrutiny because of its allergenic features. Its replacement in trinkets and spectacle frames by bronze or SiC nano-composite copper coating is underway [7].

Finally, I will mention another material used in perfectly functioning installations, replaced after a long time and large amounts of costly research, because of (obviously justified) ecological restrictions: mercury. This was long used as a depassivating agent in aluminium sacrificial anodes. It was replaced by indium, for which in turn a replacement is being sought, because of its massively increasing cost: by more than 15 times in a few years, due to its use in liquid crystal displays!

Mercury was also used successfully in antifouling paints, but for the same reasons as above, it has been replaced by a miracle product, tri-butyl tin, now becoming obsolescent in turn because of mutagenic effects on shrimps.

11.7 In synergy . . .

I have to admit that evolution in anti-corrosion technology was not merely a consequence of environmental restrictions, with no or scarce improvements in quality. I can quote at least three achievements where environmental protection went hand in hand with actual progress and innovation:

- EDP coating
- coil coating
- powder coating

It is evident to everyone that the durability and reliability of the items subjected to one of these treatments is highly enhanced, and there are considerable advantages regarding both manpower and the environment.

Of course, much other research is underway aimed at matching environmental friendliness with progress: one is the long-term effort to achieve multifunctionality (hardness, impermeability, adhesion, flexibility, gloss, self-cleaning, UV stability, etc.), possibly with a single coat.

11.8 EFC Working Party 14 on Coatings

As a matter of fact, over the years, increasing scientific and technological effort was devoted to corrosion problems, with corrosion mechanisms, passivating alloys, high-technology equipment and sophisticated test methods as the centre of interest, while scant attention was paid by corrosion science to coatings, and to organic coatings in particular. It seemed that, in general, paints were a black box for corrosionists, while corrosion mechanisms (and electrochemistry) were the paint specialists' black box.

Many years had to pass before electrochemical impedance spectroscopy (EIS) became even partially established in the paint industry, and many years before coatings became an important item within the EFC. In 1992, when Working Party 14 on Coatings (WP14) was mooted, thanks to people such as Landolt, Mercer, Weber and the EFC Board, it was still regarded by many EFC members as indicative of 'wishy-washy' thinking.

In that year, the present author actually took steps towards establishing WP14. This topic had originally fallen within the remit of WP2 on Corrosion and Protection of Steel Structures, which was, by then, moribund. Priority themes suggested for WP14 included environmentally friendly coatings and the evaluation of existing standards and specifications for coatings. In 1993, P. L. Bonora was appointed as the first chairman of WP14, which organised its first full-day session at EUROCORR '94 in Bournemouth. Two years later, the selected proceedings of its session at EUROCORR '96 became No. 20 in the EFC Series. The interests of WP14 extended to the certification of coatings inspectors in Europe, and two successful workshops on the topic, at EUROCORR '97 in Trondheim and at EUROCORR '98 in Utrecht, took place. In 1999, an international workshop on the 'Application of electrochemical techniques to organic coatings' was held at Schliffkopf in Germany, and WP14 was also involved in the organisation of a session at ISE '99 in Pavia, Italy, the proceedings of which appeared subsequently as No. 28 in the EFC Series. In 1999, Dr J. Vogelsang succeeded to the chairmanship of WP14. As early as 1995, WP14 had turned its attention to the use of electrochemical impedance in the study of corrosion protection by organic coatings, and the new chairman soon formed a task group to develop a standard for EIS, which met at Stuttgart in March 2000 and decided to undertake a collaborative test programme.

This led subsequently to the establishment by Dr Vogelsang of a new working group of the International Organisation for Standardisation, ISO/TC 35/SC 9/WG 29: 'General test methods for paints and varnishes – Electrochemical methods', which met in Pittsburgh in June 2001 and agreed to develop a joint ISO/ASTM standard for the measurement of organic coatings by EIS. The first two parts of a multi-part international standard on EIS of high-impedance coated samples (ISO 16773) have now reached the Draft International Standard stage. In 2001, Professor L. Fedrizzi (Italy) became the new chairman of WP14, which has since organised international workshops on 'Electrochemical techniques applied to organic coatings', the last three of which were held in Sintra, Portugal, in October 2003, in Villars de Lans, France, in April 2005, and in Baiona, Spain, in April 2007.

11.9 Finally . . .

Paints represent a complicated non-Newtonian multiphase system and the result of high-technology research; electro-deposited metals and alloys involve top-level scientific multidisciplinary research aimed at improving the output of a microdimensional, widely dispersed, mainly empirical galvanic industry; the application of coatings needs experts in surface technology and strict rules, which need, in turn, efficient, honest and cultured inspectors to control their proper use. Also, as I tried to outline in the above:

- paints represent one-half of the cost of corrosion;
- the sword of Damocles of eco-restrictions is always suspended above the head of the painter.

Hence, the competition between progress and ecology is like a quarrel between lovers: all stands on the doubt about whether the heart of the problem is linked to true love or if some business is hidden somewhere. I insist in believing that as, in love, reciprocal knowledge is the driving force, so, in corrosion control, the winning weapon extended awareness, together with the old and faithful war cry: I care!

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12

Fifty years of progress in the management of corrosion in the refinery industry

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12.1 Introduction

Over the last five decades, the refining industry has been a critical sector in the world economy. The main reason for this is the fact that no other industry can provide economically priced alternatives to crude oil-derived products to satisfy the energy demand. The management of corrosion has played an important part in two objectives for the development of this industry: increasing refining reliability, and lowering the cost of refining. Corrosion in the refinery industry has therefore been a major concern for the European industry and has been, since 1996, a core topic of the European Federation of Corrosion (EFC) activities following the creation of a dedicated working party.

During this period, the refinery industry has had to face major challenges in quantity, quality and safety, with important impacts on the management of corrosion of the plants. In response to the market and to environmental regulations, the quality of refining products has evolved, leading to the introduction of new or upgraded refining technologies that had to be fully resistant to corrosion. In order to increase a plant's reliability and to optimise economic savings, new management approaches for refinery plant inspection have been developed with the involvement of new monitoring techniques to provide accurate and real-time information.

To fulfil the demands for energy and transport, world refining capacities increased from about 0.5 billion tons/year in 1950 to about 4.1 billion tons/year in 2004. In response to the market and environmental regulations, the quality of refining products evolved from heavy fuels to light products with limitations on sulphur compounds. In order to handle the changes in quantity and quality demands, European refining has become more complex. Conversion capacity [fluid catalytic cracking (FCC) in particular] has been stepped up, and new hydrotreatment (HDT) (reduction of sulphur content in fuels), hydrocracking (HDC) and gasoline production units have been installed. As an example, the corrosion resistance of carbon- and low-alloyed steels, stainless steels and corrosion-resistant alloys has been investigated in wider ranges of operating conditions (temperature, pressure, flow rate, etc.) and chemical environments. The latter include both crude composition (sulphur and salt contents, heavy oil, naphthenic acids, etc.) and process chemicals (hydrogen, acid catalyst systems, etc.).

Refining plants have also faced challenges in limiting energy consumption and increasing water re-use that have impacted on the selection of economic corrosion-resistant materials and coatings and/or anti-corrosion chemical treatments. From an environmental point of view, the technologies for the treatment of acid gas emissions have required advanced knowledge of the corrosion behaviour of the equipment. In order to meet the security challenges for both people and the environment, improved corrosion monitoring techniques have been developed. New management approaches for refinery plant inspection, such as risk-based inspection (RBI) and analysis of operational feedback, have been developed. Emphasis has also been placed on knowledge transfer and the education of refinery plant staff.

Another important point is that, during the last 30 years, the number of refineries in western Europe has decreased and no replacement refineries have been built. Today, this necessitates effective management of ageing and more complex plants. The need for remaining life prediction models has also risen, requiring detailed knowledge of corrosion.

From this 50-year review of the transformation in the corrosion management of refineries, some trends for the next few years will be proposed.

12.2 The impact of quantity requirements on refined oil products: 1955–2005

In Europe, the World War II damaged or destroyed many refineries. In order to fulfil the economic growth demand, refineries were built or re-equipped between 1945 and 1975. As indicated in Table 12.1, which presents data obtained from [1–8], the capacity to produce refined oil products in Europe increased greatly between 1950 and 1980, at which point production reached a maximum of about 1170 million tons/year.

Since 1980 there has been a slight decrease in the output of European refineries, with the shutdown of some refinery plants and ageing of others. The refinery industry has been operating in a difficult environment over the last two decades: there have been only a few years since the early 1980s in which refineries produced decent returns on investment. As a result, capital investment decreased; as an example, only one new plant has been completely rebuilt in Europe (the Leuna refinery in Germany). The current distribution of refinery capacities in most European countries is shown in Table 12.2, and the number of production plants is given in Table 12.3 [1–4]. Italy and Germany produce the largest quantities of refined oil products, with 17 plants and 16 plants, respectively.

Table 12.4 [1–4] shows that in 2004, Europe manufactured 20.5% of the world's refined oil products while utilising 18.5% of world refinery capacity.

These figures highlight the relationship between industrial development and the consumption of crude oil-based energy products. Refining capacity has been developed to satisfy these energy requirements.

Table 12.1 Refinery capacity (millions of tons per year)

	Europe	North America	World
1950	50	345	525
1970	780	667	2330
1980	1170	1024	4116
2004	847	940	4121

Table 12.2 Refining capacity in Europe in 1950, 1970, 1980 and 2004

Country	Capacity (millions of tons/year)			
	1950	1970	1980	2004
Austria		8	12.5	10.5
Belgium	0.715	35.2	53	40
Bulgaria			15	5.7
Croatia			14	12.5
Czech Republic			12.5	9.9
Denmark	0.031	9.8	10.7	8.8
Finland	1	8.7	16.8	12.6
France	18.15	127	167	98
Germany	>5.6	>127	175	116
Greece		5.1	21	20
Hungary			16	8.05
Ireland	0.03	2.7	2.8	3.55
Italy	5.75	185	204	116
Lithuania				13.2
The Netherlands	4.9	69.6	91	61.4
Norway	0.05	10.1	13	15.5
Poland			19	17.5
Portugal	0.375	4.2	17	15.2
Romania			31	25.8
Slovakia			10	9.9
Spain	0.285	42.3	74	63.6
Sweden	1.24	11.8	22.5	21.7
Switzerland	0.1	5.1	5.1	6.6
UK	12.57	120	131	91.3
Total	>50	>671	1170	847

In order to produce ethylene (a primary compound in petrochemical manufacturing), steam cracking units have been installed in some refineries. In Europe, the first steam crackers were built for a low production rate (6000 tons/year of ethylene) by 1940, and in the UK by 1946. To follow the economic development of the petrochemical industry, the number of steam crackers and their capacity continuously increased between 1960 and 1985, as indicated in Table 12.5 [6].

From 1980 to 2005, the doubling of the western Europe ethylene capacity was mainly achieved by increasing the performance of existing units by:

- increasing the furnace capacity;
- increasing the selectivity by using low resident time processes;
- using more high-temperature corrosion-resistant alloys in order to increase the temperatures of the furnace tubes.

From a corrosion point of view, two periods can be distinguished for the European refinery industry:

- From 1950 to 1980, many new plants were built, and the main objective was to respond to the sharp increase in European consumption.
- From 1980 to the present, consumption has slightly decreased in Europe; refineries have been closed, and the operating ones have had to face new challenges

Table 12.3 Number of refineries in Europe in 1950, 1970, 1980 and 2004

Country	Number of refineries			
	1950	1970	1980	2004
Austria		2	1	1
Belgium	7	7	7	5
Bulgaria			1	1
Croatia			5	3
Czech Republic			5	4
Denmark	3	3	3	2
Finland		2	2	2
France	16	24	22	13
Germany	30	35	32	16
Greece		2	4	4
Hungary			5	2
Ireland	1	1	1	1
Italy	16	36	32	17
Lithuania			1	1
The Netherlands	2	7	8	6
Norway	1	3	4	2
Poland			9	5
Portugal	1		2	2
Romania			13	10
Slovakia			2	1
Spain	2	8	9	9
Sweden	4	5	6	5
Switzerland	1	2	2	2
UK	22	21	19	11
Total	106	158	195	125

Table 12.4 Worldwide refining capacity in 2004

	Refining capacity in 2004 (millions of tons/year)	Number of refineries in 2004
Europe	847	125
North America	940	153
Russia	271	42
Japan	235	33
China	232	95
India	112	17
World	4121	717

Table 12.5 Western Europe ethylene production capacity

	1960	1970	1985	2005
Western Europe capacity (1000 tons/year)	700	7000	12 500	20 000
Average capacity by unit (1000 tons/year)	15–20		250–300	

with regard to both cost of production (due to the increase of the price of oil) and quality, in order to meet demands for new petroleum types and to conform with environmental regulations.

12.3 Impact of quality requirements on refined oil products: 1955–2005

Between 1920 and 1950, many processes were developed in order transform the products of crude oil distillation into refined end-products: thermal cracking, thermal reforming, and then catalytic cracking and alkylation with sulphuric or hydrofluoric acids. The objectives of these processes were to manufacture the products required for heating, electricity production, and transportation (automotive, planes), and also for producing feedstock for the emerging petrochemical industry.

For the construction of new refining units, the primary materials recommendations were based on observed corrosion resistance.

Then, until 1975, in order to improve the efficiency of the processes and the quality of the products, catalysts and the use of hydrogen came to the forefront in refining through several new processes:

- new catalysts for the reforming process
- increase in the use of hydrogen for isomerisation, hydrodesulphurisation (HDS), HDC, and hydroconversion

As will be presented in more detail below, the resistance of steels to the adverse effects of hydrogen were investigated during this period, with the introduction of innovative grades of low-alloy steels.

Over the last 30 years, refining has suffered an unsettled time, with two oil crises, the Gulf wars, and growing environmental awareness.

In market economy countries, the profile of the consumption of refined products changed significantly during these years, as indicated in Table 12.6 [9].

The heavy fuel sector dropped rapidly from 30% to 13%; in contrast, the proportion of light products, especially the middle distillates (jet fuels and gas oils), increased. To handle these changes, European refining has become more complex, with the introduction of conversion capabilities such as FCC and HDC. These processes have resulted in new corrosion challenges.

To limit environmental impacts, more stringent specifications on sulphur content have been applied to gasoline and diesel fuels, as indicated in Tables 12.7 and 12.8 [10].

Table 12.6 Development of the demand in petroleum in the market economy countries

	1970		1980		1990		2000	
	10^6 tons	%	10^6 tons	%	10^6 tons	%	10^6 tons	%
Gasoline	492	25.4	626	26.6	750	26.8	876	26.2
Middle distillates	530	27.4	721	30.6	950	33.9	1163	34.8
Heavy fuels	608	31.4	645	27.4	500	17.9	426	12.8
Others	307	15.8	363	15.4	600	21.4	875	26.2
Total	1937	100	2355	100	2800	100	3340	100

Middle distillates: jet fuels, heating oil, diesel oil. Others: refinery gas, liquefied petroleum gas, naphthas, solvents, lubricants, wax, bitumen, petroleum, coke.

Table 12.7 Evolution of the gasoline specification

Gasoline	1996	2000	2005	2005–2010
Sulphur (p.p.m.)	500	150	50	10–30
Benzene (%)	5	1	1	< 1
Aromatics (%)	Not specified	42	35	< 30
Olefins (%)	Not specified	18	8–18	< 10

Table 12.8 Evolution of the diesel fuel specification

Diesel fuel	1996	2000	2005	2005–2010
Sulphur (p.p.m.)	500	350	50	10–30
Cetane (%)	49	51	51–58	53–55
Polyaromatics (%)	Not specified	11	2	1–2

To fulfil these specifications, new HDT, HDC and gasoline production units have been installed in Europe.

In summary, over the last 30 years, European corrosion specialists have had to take account of improved HDT and FCC processes.

Another requirement has been the need to have clean processes producing clean products to reduce polluting gaseous, liquid and solid discharges. Improved gas and water treatments have been installed with, most often, more corrosive media (such as CO_2 and H_2S acid gas) to be handled and transformed.

12.4 Impact of the quality of crude oils

During the last 50 years, large changes in the sources of crude oil have occurred in order to supply the increasing demand for refined petroleum products. Many European refineries were constructed in the period 1950–1960 for non-corrosive crudes (typically Sahara crudes). Then, their source may have been changed to the Middle East (Arab light), North Sea, Safaniya (bituminous type), Russia, Venezuela, or Nigeria. As the composition of the crude differs from one oil field to another, this has impacted on the corrosion tendencies of some refinery equipment. For example: the chloride, sulphur and naphthenic acid contents of a specific crude oil can affect the corrosion performance of a refinery.

12.4.1 Chloride

Desalting processes had to be improved and oil tank water separation methods optimised in order to operate with higher quantities of mineral chloride. Various combinations of ammonia and chemical injection (neutralising and filming inhibitor) have been developed [11,12]. In addition to the usual inorganic (magnesium and calcium) chlorides, some organic (termed phantom) chlorides can also enter refinery facilities [13]. These chlorides are not detected in the salt in crude extraction and titration, but they can also cause the formation of hydrogen chloride. Possible sources of phantom chlorides include chlorinated solvents used in upstream operations, refinery slops, recycled lubricating oils, and contamination en route to the refinery.

12.4.2 Sulphur

This compound uniformly corrodes steels at high temperature, and extensive prediction studies have been performed in order to select the required composition of steels with regard to the temperature and quantity of hydrogen [14–17].

For more severe conditions of sulphidation, stainless steels are commonly selected, for instance, for HDS, HDT and FCC plants. During periodic shutdowns or start-ups, or during operation when air and moisture are present, stress corrosion cracking (SCC) of sensitised austenitic stainless steels can occur due to the formation of polythionic acids. The latter are formed as a consequence of the reaction of metallic sulphides with water and oxygen. To avoid such degradation, refinery corrosion specialists have developed specific shutdown procedures and specific recommendations for the protection of austenitic stainless steels [18–23].

12.4.3 Naphthenic acids

Some crudes from Russia, Venzelua, India or Angola contain appreciable quantities of naphthenic acids. Naphthenic acid corrosion (NAC) of crude vacuum units can occur when the crude being processed has a significant neutralisation number (>0.1 mg KOH/g without sulphur) and the temperature is between 220 °C and 430 °C [24–29]. During the last 50 years, certain rules of thumb have been defined by corrosion engineers to deal with the problem of NAC. Extensive work has also been carried out in order to provide a better understanding of the relationship between corrosion and the different naphthenic acids present in corrosive crudes. Corrosion management experiences have resulted in improved material specifications for stainless steels of the AISI 316L and 317L types. Specific corrosion inhibitors have also been developed. A very complete review of the literature on this topic has been performed by G. Gabetta *et al.* [30]; the references of this review can be downloaded from the 'EFC WP15 – refinery corrosion literature' database developed by H. J. de Bruyn [31].

12.5 Impacts of new processes and new process conditions

New processes or process upgrades that have been installed in European refineries have had a major impact on corrosion management studies. Some of the most representative ones are reviewed below. Refinery corrosion specialists are, however, faced with many others as well.

12.5.1 High-temperature hydrogen attack

During the last 50 years, hydrogen has been increasingly used in process units in order to meet the new gasoline and fuel specifications as well as for heavy oil conversion (which can be achieved in HDC plant operating at more than 150 bar of H_2) and reduction of the sulphur level (obtained by HDC, HDT and HDS treatments). Under higher temperature and higher hydrogen pressure ranges, carbon- and low-alloyed steels may suffer high-temperature hydrogen attack (HTHA). This is due to the reaction of atomic hydrogen that diffuses through the steel with the carbides in the steel to form methane [32–34]. As methane cannot diffuse through steel, pressure builds up and leads to the formation of blisters and/or cracks. In order to improve the carbide stability of pressure vessel steels, special low-alloy steels containing chromium and molybdenum have been developed; vanadium and tungsten are also added, in order to increase the mechanical properties of these steels.

On the basis of their experience, end users of these steels have defined a design practice for each grade of steel [32]. This is periodically reviewed, and as a consequence, the borders for acceptable process conditions or the exclusion of steel grades such as C–0.5Mo have been published.

Extensive studies have also been and are still being performed in order to evaluate the remaining lifetime of aged equipment under hydrogen at high temperature [34]. For these predictions, the ageing of these low-alloy steels due, for example, to temper embrittlement in the case of 2.25Cr–1Mo steel, is always an important issue.

For low-alloy steel reactors with internal protection by stainless steel cladding, high local concentrations of hydrogen can occur at the interface of the two alloys, as hydrogen does not have the same diffusion rate in both categories of steels. This may lead to disbonding of the internal stainless steel lining upon cool-down. Specific shutdown procedures have been developed in order to avoid such disbonding problems [35].

12.5.2 Carbonate SCC

During the last 20 years, carbonate SCC has become active in FCC units [36]. In that time, there have been significant process changes in FCC refining technology to enhance unit operation, leading to a decrease of sulphur content and to an increase of nitrogen and CO_2, and resulting in an increase of the pH of the sour water. With these new conditions, SCC of carbon steel can develop within only a few months [37].

12.5.3 High-temperature carbon attack

The increase of temperature and carbon activity in processes such as reforming or steam cracking has led to more severe conditions of coke plugging, carburisation and metal dusting. Better understanding of the mechanisms of these degradation processes has permitted improved solutions to be developed and the process requirements to be achieved.

12.5.4 Coke deposits

The formation of carbon deposits, which occurs at carbon activities $a_c > 1$ in the temperature range 450–1100 °C, has become a major problem in petrochemical and refinery processes [38–46]. Carbon deposition on reactor walls causes localised disruption of processes due to heat transfer reduction and pressure drops. Excessive carbon deposition causes the deterioration of furnace alloys due to significant migration of carbon into the alloys, and incurs high cleaning costs to remove the coke from the surface.

Different mechanisms of coke formation have been identified. These are mainly dependent upon the temperature and the alloy composition. A catalytic heterogeneous mechanism occurs at temperatures between 450 °C and 700 °C, with the formation of carbon filaments being catalysed by some components of the alloy (Fe, Ni or Co). At higher temperatures, a pyrolitic homogeneous process occurs, mainly controlled by the composition of hydrocarbons [41]. During the last 20 years, coke deposition has disturbed some catalytic reforming processes that treated sulphur-free cuts [45]. To limit coke deposition and improve process efficiencies, specific alloy metallurgy, coatings (mainly based on chromium, aluminium or silicon) or chemical inhibitors (such as sulphur compounds) have been studied and developed [46].

12.5.5 Carburisation

At high temperatures, carbon (from hydrocarbons, coke, and gases rich in CO and CO_2) can diffuse into an alloy: solid-state carbon saturation occurs, followed by the formation of metallic carbides [47–49]. Carburisation occurs in refinery and steam cracking furnace tubes when excessively high temperatures are involved (due to the furnace configuration or to the formation of a coke layer acting as thermal insulation). This can result in the loss of high-temperature creep ductility, loss of ambient temperature ductility, and loss of both weldability and corrosion resistance. The main forms of damage that have been encountered involve the formation of grooves and cracks. During recent decades, metallurgists have manufactured new grades of refractory alloys that possess better resistance to carburisation, due to their higher contents of nickel, chromium and other elements (aluminium, silicon), which can also act as strong oxide or sulphide film formers [49].

12.5.6 Metal dusting

During the last 30 years, some failures associated with localised pitting-type morphology have occurred due to metal dusting [43,44,47,49–51]. Metal dusting has been observed in catalytic reforming furnace tubes, cokers, methanol reforming units and hydrodealkylation furnaces and reactors. Metal dusting is a form of carburisation resulting in accelerated localised pitting, which occurs mainly between 450°C and 850°C, in carburising atmospheres and process streams containing carbon and hydrogen. Metal dusting is preceded by carburisation and is characterised by rapid metal wastage (metallic ‘dust’ particles). To avoid such disruption, use can be made of alloy compositions that are more resistant [51], but the application of a chromium- or aluminium-based diffusion coating and the presence in the carburising atmosphere of a sufficient amount of sulphur are also remedies that have been extensively studied in laboratories and in plants [45].

12.5.7 Acid corrosion in alkylation processes

Acid alkylation processes were developed between 1920 and 1950, and many of them had been installed in European refineries by 1985. These processes alkylate light olefin fractions (butenes from FCC or visbreakers) with isobutane, using sulphuric acid or hydrofluoric acid as a catalyst to produce gasoline. During the last 50 years, refiners have had to manage the safety and the performance of these processes, where very corrosive catalysts are involved.

Hydrofluoric acid alkylation

Hydrofluoric acid can cause high general corrosion rates and may also act as a hydrogen promoter, leading to hydrogen-induced cracking and stress-oriented hydrogen induced cracking (SOHIC). In order to select more resistant materials, many investigations have been performed, leading to the successful use of carbon steel and Cu–Ni (alloy 400). Recommendations for specific compositions and mechanical property limitations have been developed. As an example, due to the formation of a protective iron fluoride scale, carbon steel with a low concentration of residual elements (%Cu + %Ni + %Cr < 2.2%) is resistant in nearly all anhydrous HF conditions [52–56].

Sulphuric acid alkylation

The limits of corrosion resistance of the main alloys have been investigated for different ranges of acid concentration, temperature, and flow velocities. For carbon steel, the conditions under which a protective iron sulphate layer is active have been investigated (concentration > 85%, temperature < 40°C, velocity < 6 m/s). For more severe conditions, nickel-based alloys (such as alloy B2, C276) have been developed [57–59].

12.6 The impact of environmental requirements on acid gas and water treatment units

As mentioned earlier, from 1955 to today, refineries have been required to synthesise more environmentally friendly refined products, using processes with lower environmental impacts. New treatment units dealing with more aggressive media have had to be built, and corrosion challenges have had to be faced, dealing, for example, with acid gas.

12.6.1 Treatment of acid gases in amine units

The removal of acid gases (CO_2, H_2S) from refinery gas streams using amine-treating units has never been considered a problem-free technology, despite the fact that it has been used in industry for over 50 years. Originally, monoethanolamine, diethanolamine, methyldiethanolamine and proprietary solutions containing monomethylethanolamine or di-isopropanolamine were used. The process can be subject to a number of operational difficulties, the most severe of which is corrosion of the process equipment. Because of the tremendous impact of corrosion, it is necessary to suppress corrosion to an acceptable level in amine-treating units. Two types of corrosion mechanism have had to be overcome for carbon steel: amine SCC and uniform (or sometimes local) loss of thickness. Corrosion studies have pointed out that this second type is not due to the amine itself, but results from the dissolved acid gas and from the amine degradation products [60–63]. The first type of corrosion was responsible for a fatal accident at the Chicago plant of Union Oil in 1984, where no stress relief heat treatment was performed following a repair [63,64]. Extensive investigative work has therefore been carried out all over the world. A typical example in Europe is the EFC Working Party 15 (WP15) amine corrosion survey [65].

The corrosion problems have been mitigated by several approaches, including: (a) the use of appropriate equipment design; (b) the use of corrosion-resistant materials such as stainless steel of the AISI 316 type instead of carbon steel; (c) the removal of solid contaminants from liquid solution; and (d) the use of corrosion inhibitors.

12.6.2 Treatment of water

During recent decades, more and more severe environmental constraints have prompted refiners to assume a rational approach to water treatment and to take more restrictive steps concerning its disposal. Limitations on the use of fresh water supplies have imposed more requirements for recycling of water. This re-use decreases the amount of water consumed and to be disposed of, but increases the risks of corrosion damage and scale deposition.

Thus, even if the water is initially clean and non-corrosive, because of this concentration effect it becomes corrosive, due to very high residual concentrations of various species and their tendency to induce scaling and biofouling [66–69].

Refineries were faced with the double challenge of having to deal with more corrosive, more heavily scaling water using environmentally friendly inhibitors with efficiencies as high as those of the previous generation. In order to provide improved knowledge and guidance on this subject, working groups of CEFRACOR and the EFC (WP15) have exchanged experience and have published their work in EFC No. 40, *Control of Corrosion in Cooling Waters* [70].

12.7 Benefits of new materials, coatings and inhibitors in refineries

Over the last 50 years, extensive studies have been carried out on materials, coatings and inhibitors with the aim of limiting the effects of corrosion. As an example, to increase the mean time between the replacement of equipment, corrosion rate allowances were decreased from 0.35 mm/year in 1940 to 0.05–0.1 mm/year in 1980 [78].

12.7.1 Progress in materials

Although carbon steel still accounts for more than 80% of all materials used in refinery equipment, much progress has been made with this type of material and also on the development of more corrosion-resistant alloys.

In the case of carbon steel, the metallurgical industry has developed improved manufacturing deoxygenation processes to produce killed steels with more homogeneous microstructures. Better control of the concentration of residual elements has provided improved corrosion cracking resistance, e.g. against hydrogen embrittlement in wet H_2S media. For this application, the metallurgical improvements resulted in the publication of international materials recommendations [70–72]. As already mentioned, new grades of low-alloy steels containing various quantities of Cr, Mo, V and W for better HTHA resistance and improved mechanical properties have been developed.

During the last 50 years, new grades of stainless steels and nickel alloys have also become available. Among many other applications, because of their resistance to localised corrosion and their good mechanical properties, duplex stainless steels have been successfully used for heat exchangers in crude units, reactor effluent air coolers in HDT plants, and waste water treatment units [73].

Titanium alloys have also been used to overcome specific corrosion problems for condensers in FCC overheads and sour water strippers [74].

For severe corrosion problems, such as in the injection lines used for catalyst regenerator chemicals in reforming units or in the tower tops of crude distillation units, high-grade nickel-based alloys have successfully replaced stainless steels or conventional Ni–Cu grades [75,76].

12.7.2 Progress in coatings and cladding

The combination of the specific properties of two materials has solved, in a cost-effective way, corrosion and design problems for the refinery industry. Metallic cladding is extensively used for HDT and HDS reactors; the stainless steel inner layer gives good resistance to high-temperature sulphidation, and the low-alloy steel outer part provides mechanical strength [77]. Different cladding processes have been developed: roll bonding, explosive bonding, and weld overlaying.

12.7.3 Inhibitors

The refinery industry benefited greatly from developments in the inhibitor sector, which mainly occurred between the late 1940s and the late 1960s, first for the oil and gas production sector, and later for refining.

Improvements have overcome the adverse features of the earliest corrosion inhibitors, resulting in better solubility and the avoidance of emulsion formation [78]. By 1960, the main families of corrosion inhibitors had been developed, and were based on long-chain hydrocarbon molecules that terminate in nitrogen groups, such as amines, amide, imidazolines and quaternary amines [79]. From the 1980s, developments of refinery corrosion inhibitors have mainly continued in the fields of NAC [80] and the control of corrosion in cooling water systems. In the latter application, the objective is to develop more environmentally friendly chemicals [70,81,82].

Neutralisation procedures have mainly been developed to reduce corrosion by HCl in crude unit overhead systems. Ammonia was the first neutraliser tested during the 1940s, followed by caustic compounds (1950s) and liquid organic agents (1960s) in order to overcome the deposition of ammonium salts.

Fouling also occurs in quite a number of refinery processes, but mainly on heat exchanger surfaces; the deposits induced by fouling are an important cause of under-deposit corrosion damage. To avoid such problems, specific formulations have been designed that are built around a dispersant package with antipolymerants, oxygen scavengers, metal deactivators and corrosion inhibitors [79].

Economic considerations were also an important factor in the development of inhibitors. For a refinery, depending on the extent to which they are applied, process additives cost from $20 to $50 per 1000 barrels of refinery charge capacity [79]. During the last decade, in order to reduce this cost, many performance treatment programmes, developed by the suppliers of additives, have been launched and evaluated by end users.

12.8 Application of progress in monitoring techniques to corrosion control in refineries

The monitoring of corrosion in refinery plants is a field in which much progress has been achieved through the improvement and the development of new destructive or non-destructive [non-destructive evaluation (NDE)] techniques. The purpose and methods of corrosion monitoring have changed from the early days of weight loss coupons and visual inspections.

New technologies based on accurate systems for detecting the physical, chemical and electrochemical properties of the material, the corrosive media and their interface appeared. These developments, together with improved inspection methods, have been responsible for many economic benefits [83–85].

Destructive corrosion monitoring techniques have benefited from improvements in analytical (e.g. the sensitivity of chemical analysis of materials) and mechanical test methods.

Fifty years ago, most of today's NDE techniques did not exist. Now, some of these can be used without internal access to the equipment (non-intrusive NDE). As a non-exhaustive list, these methods include:

- manual, automatic, guided-wave or long-range ultrasonic testing to evaluate thickness;
- pulsed-eddy current testing for thickness measurement;
- acoustic emission to evaluate and locate active corrosion areas;
- profile and real-time radiography to evaluate defects;
- magnetic flux leakage analysis to detect defects;
- hydrogen flux measurements for corrosion evaluation.

Some of the intrusive methods that have been developed are:

- metallographic replication and hardness testing to characterise the microstructure and the mechanical properties of the material;
- wet fluorescent magnetic particle testing to detect defects;
- electrochemical methods (polarisation resistance or impedance or noise analysis) to evaluate corrosion rates.

The combination of several of these control and monitoring techniques, in connection with improved inspection strategies, has been an important element of progress in achieving improved reliability together with cost savings in the refinery industry.

12.9 Advanced inspection plans

In association with improved monitoring systems, advanced inspection strategies have been developed and implemented during the last 50 years. The primary objective of these strategies is to reduce the number and frequency of unplanned shutdowns. To achieve this objective, the inspection programmes moved from a strategy mainly based on the consequences of the plant's degradation to a strategy more dedicated to the causes and the development of the degradation. This approach has led to more selective opportunity and on-stream inspection programmes instead of comprehensive routine inspections at fixed time intervals. This required an accurate knowledge of the 'real life' of a unit. Refining companies have developed strategies relying on RBI programmes, using risk as a basis for prioritising and managing the inspection programme, where the items of equipment to be inspected are ranked according to the risk associated with their failure [34,83,86].

In nearly every situation, once risks have been identified, alternative opportunities are available to reduce them. The purposes of the RBI programme are summarised as follows:

- Screen operating units within a plant to identify areas of high risk, estimating a risk value associated with the operation of each equipment item in a refinery or chemical process plant based on a consistent methodology.

- Prioritise the equipment on the basis of the measured risk.
- Design an appropriate inspection programme.
- Systematically manage the risk of equipment failures.

The risk associated with the failure of operating equipment has been defined as the combination of two separate components: the consequence of failure and the likelihood of failure. For consequence calculations, safety, monetary loss and environmental impact are included.

The analysis of failure likelihood is based on a generic database of failure frequencies by equipment types that are modified by two factors that reflect identifiable differences from 'generic' of the equipment item being studied.

To conclude, the benefits of these new advanced inspection strategies are cost savings (for instance by adaptation of the shutdown periods), increased safety, and better control of environmental impacts. Typically, the average unplanned downtime has been reduced to approximately 4% of the plant running time [87].

12.10 Training and development and exchange forums

During the last five decades, the training and development of personnel dealing with material degradation have been considered to be important factors for the management of corrosion in the refinery industry. At international and national levels, specific corrosion education courses have been implemented, not only for plant inspectors but also for unit maintenance and operating personnel. Many national safety regulation authorities now require corrosion-related qualification grades for personnel working in the inspection departments of refinery and petrochemical plants.

Exchanges of information on corrosion degradation and field experience have also been developed between specialists dealing with corrosion and materials in refineries in order to share and extend failure databases. Many similar refinery process units are installed all over the world, and sharing information is an important factor in reliability and safety.

The creation in 1996 of a working party dedicated to corrosion in refineries under the auspices of the EFC is an example of the establishment of one such exchange forum. Another objective of these groups is the development of documents, guidelines and publications that reflect a consensus approach to refinery corrosion problems between the main European refining and petrochemical companies [88].

Other national and international networks have also grown in order to fulfil the performance and safety targets of the refinery industry. In the USA, the National Association of Corrosion Engineers (NACE) has created several technical committees on specific aspects of corrosion in refineries. In France, a network called GEMER (a group to study materials used in refineries) was launched in 1956, and has since organised seminars regularly in order to exchange information on corrosion and field experience. As another example, in Italy, a local NACE section is also dedicated to this topic. Petroleum companies also organise their own national and international corrosion networks and seminars.

12.11 Conclusions and the future

Much progress has been achieved during the last five decades in order to ensure the safe and economical expansion of this industry (Europe has doubled its refining capacity). However, the impact of corrosion on the refinery industry is still of great concern: as an example, for 22% of the world's refining capacity, the annual cost of corrosion for the US refinery industry was US$3.7 billion in 1998, representing 2.7% of the total cost of corrosion in the USA [89]. In 1980, an API study evaluated the main sources of refinery incidents as [90]:

1. equipment failure, 28%;
2. human error, 28%;
3. faulty design, 13%;
4. inadequate operating procedure, 11%;
5. insufficient inspection, 5%;
6. process upset, 2%;
7. inadequate education, 13%.

Corrosion aspects are involved in points 1, 5 and 7 of this classification, and still represent a major contribution to incidents in the refinery industry.

For the future, new corrosion challenges will have to be faced in order to reduce further the rate of incidents due to corrosion while allowing further development of the refining industry. Refining and petrochemicals can be considered in certain respects to be mature industries, but they are constantly changing. Faced with the complexity of demand for refined products, the interaction between refining and petrochemicals will continue to strengthen.

Also, in order to face future uncertainties over the availability of crude oil, refineries should be able to treat not only oil but also gas in new production plants for synthetic fuels from gas (e.g. gas-to-liquid Fischer Tropsch synthesis from syngas). To meet the future gasoline and fuel composition requirements, the hydrogen demand in refineries could require the implantation of new hydrogen production facilities (using partial oxidation or a steam reforming process), with their specific corrosion problems. The refining and petrochemical plants should continue to limit the emission of traditional atmospheric pollutants such as sulphur and nitrogen oxides, but also of greenhouse gases, in particular CO_2. The technologies to be used would require, as shown by refinery experience, new knowledge related to corrosion resistance. All of these developments will continue to rely on further progress in the science and technology of corrosion and its management in the coming decades.

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13
Half a century of progress in cathodic protection

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13.1 Introduction

Cathodic protection is a very effective electrochemical method for preventing corrosion in mildly corrosive continuous electrolytes, provided that it can be implemented under good conditions. Nowadays, galvanic systems as well as impressed current systems are well known and used in many industrial and non-industrial applications, such as pipelines, marine, coastal and offshore structures, reinforced concrete structures, insides of vessels, or buried and above-ground tanks.

The celebration of the Golden Anniversary of the European Federation of Corrosion (EFC) constitutes a good opportunity to take a look back at EFC Working Party 16 on Cathodic Protection (WP16) and present an overview of progress in this field during the past 50 years. One of the purposes is to remind the younger corrosion engineers that, not such a long time ago, the science and technology of cathodic protection was still considered somewhat mysterious and that many potential users were sceptical about its effectiveness. The basis of the present survey comes from the author's own experience and documentation and from contacts with leading cathodic protection experts in European countries and abroad, aimed at collecting information. The survey presented here has been prepared with the best knowledge and information available. However, such a task is not easy, because the written historical documentation is scarce, and direct information concerning the 'first ages' has now disappeared. Mistakes or forgotten points are not only possible but certain, and the author would like to be informed of any further corrections or additions.

The first part of this survey provides a snapshot of the origins of this technique and the status of its application 50 years ago in various European countries and in other parts of the world. It appears that in 1955, when the EFC was founded, cathodic protection was mainly applied to protect the hulls of warships and the first gas pipelines.

The second part summarises the major advances made in the use and knowledge of cathodic protection during the past half-century in the same countries, accompanying developments in industry (oil and gas, chemicals), transportation and the infrastructure (marine activities, harbours, water industry), and private activities (buried propane tanks, water heaters, swimming pools). The measurement techniques and the methods used to verify the effectiveness of protection and of the galvanic anode behaviour are especially addressed in the survey. The evolution of technology, recommended practices, standardisation and regulations is also presented.

Finally, the present situation is analysed, especially through the status of European and international standards and recommended practices. The need for qualification and certification of cathodic protection personnel is emphasised. The field that appears to necessitate the most significant progress is discussed: how to assess and, if possible, improve the effectiveness of cathodic protection beneath disbonded coatings on buried pipelines.

13.2 The EFC and cathodic protection

Papers relating to cathodic protection issues have been presented during the former European Corrosion Congresses and the current EUROCORR conferences during sessions organised by various working parties. However, a working party fully dedicated to cathodic protection (and associated coatings), WP16, was launched only recently, on 29 September 1998, during EUROCORR ’98 in Utrecht (The Netherlands). The main goals decided on were to work on certification in cathodic protection, organise scientific and technical discussions and technical symposia in all cathodic protection application sectors, and prepare EFC publications. The first session organised by WP16 took place at EUROCORR 2000 in London.

A document on ‘Qualification and certification in the field of cathodic protection: Present situation and possible European scheme’ was issued in May 2001, and copies were made available on request. This action continued through the preparation by CEN TC219/WG5 of the European standard EN 15257:2006, specifying a general scheme on ‘Cathodic protection – Competence and certification of cathodic protection personnel’. The main objective is now to prepare an EFC publication entitled *A State of the Art Report on the Assessment of Cathodic Protection of Buried Pipelines*. WP16 meets at least once per year, in conjunction with EUROCORR.

13.3 The origins of cathodic protection

13.3.1 The first ages

The benefits of galvanic coupling of metals for the most ‘noble’ component of the couple were probably put into practice for a long time without the reasons for such a phenomenon being known. In a paper given to the Accademia dei Georgofili of Florence in 1792, Giovanni Fabbroni was the first to describe bimetallic corrosion [1]. In 1802, Alessandro Volta was the first to express the basic principles of galvanic cathodic protection, describing the effect of a direct electric current on oxidation of metals: ‘The oxidation increases very much on the metal from which the current goes out for entering in water or any other oxidising liquid. The oxidation decreases or entirely suppresses it on metal into which current enters and on which hydrogen is evolved’ [2]. In 1806, Humphrey Davy advanced the beneficial effect on corrosion of copper in sea water of contact with zinc, tin or iron [3–5].

13.3.2 The first galvanic cathodic protection system

The first well-known application of cathodic protection with what is now called a ‘galvanic cathodic protection system’ using ‘sacrificial anodes’ dealt with sea water, which is an ideal environment for implementing this technique, due to its high conductivity and homogeneity and to its corrosivity for iron and steel, which renders it unacceptable for long-term applications. The details of this first historical use of cathodic protection have been presented recently by Professor David Scantlebury [6].

After receiving a commission with the British Admiralty in 1824, the future Sir Humphrey Davy established within 2 years the basic principles of cathodic protection (including the possibility of using impressed current) and studied especially the use of iron and steel for the protection of copper, the influence of dissolved oxygen, the effect of the area ratios, and the possibility of preventing galvanic corrosion of steel by coupling it to copper. Professor Scantlebury explains that:

> He conducted a full scale ship's trial on the SS Samarang, a wooden war ship which had had a copper bottom fitted three years previously and where the copper was showing signs of corrosion. He fitted four cast iron anodes, two at the bows and two at the stern at one eightieth of the area of copper and the ship sailed to Nova Scotia and back returning in January 1825. He noted full protection of the bows and stern but some copper corrosion towards the central part.

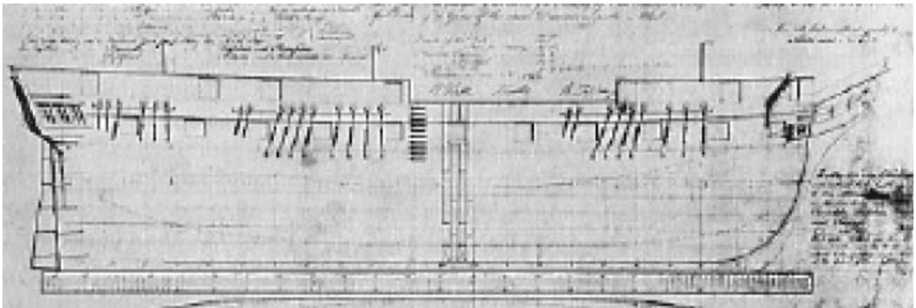
Figure 13.1 reproduces the drawing of the first galvanic cathodic protection system.

Davy also performed another trial on a cargo ship called the *Carn Brea Castle*, and described the newly coppered bottom as 'perfectly bright' with a 'beautiful and polished surface' after the ship had returned from Calcutta. This is assumed to be the first deliberate galvanic cathodic protection application at an experimental level. 'Electrochemical means' was the wording used. Installation of iron plates to protect copper sheathings on wooden ship hulls of the British Royal Navy warships was then introduced. Subsequently, zinc replaced iron, allowing galvanic protection of steel. The actual effectiveness of this system was certainly low, due to the lack of purity of the zinc used. The law established by Faraday in 1829 for quantifying electrolysis represented a major advance in explaining and sizing galvanic systems.

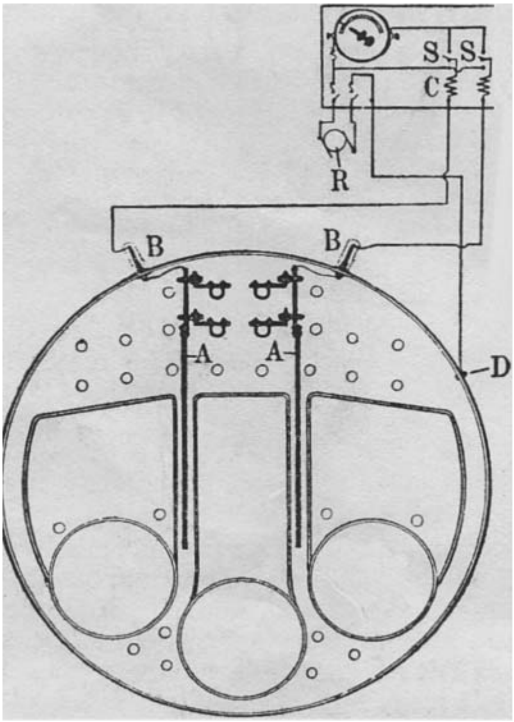
In 1865, Antoine Becquerel, member of Institut de France, studying the protection of armour plates on ships with zinc, wrote that 'another use could be made with a chance of success: This deals with the preservation of cast iron pipes buried in wet soils' [7].

13.3.3 The first impressed current cathodic protection system

The first application of impressed current cathodic protection (ICCP) seems to have been for preventing (galvanic) corrosion together with scale in boiler condensers used



13.1 First trial of galvanic cathodic protection on a warship by Sir Humphrey Davy

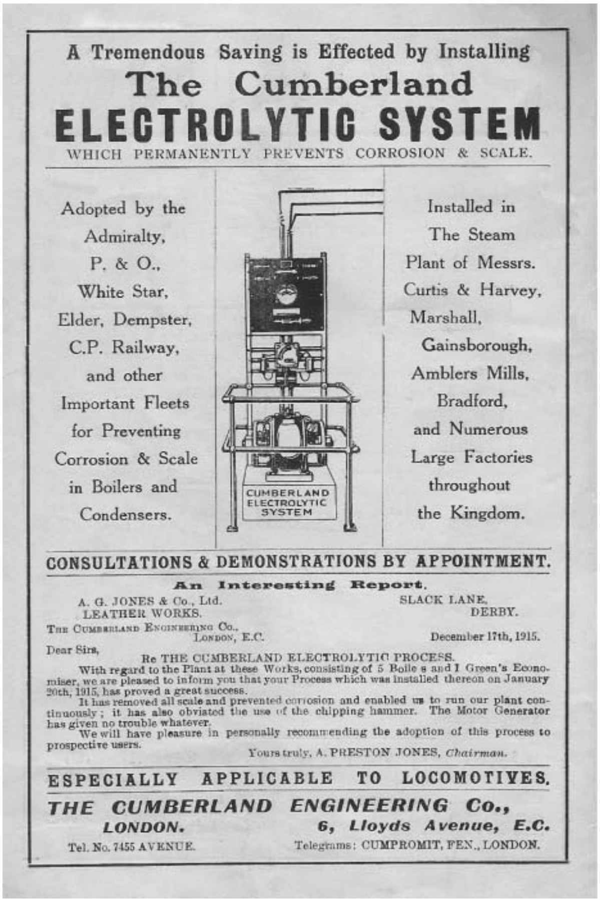


13.2 Application of the ‘Cumberland electrolytic system’ in a boiler. AA, iron anodes; BB, insulated shell bolts (positive); CC, resistance coils; SS, two-way switches; D, negative connections on shell; R, electrical generator

for steam-driven engines at the end of the 1900s. A paper published in Australia in 1910 presented the industrial tests carried out to study this new method [8]. Soft iron was used for the anodes, and current was supplied by low-tension dynamos generating a continuous current under a voltage of 6–10 V. This process, called the ‘Cumberland electrolytic system’, was introduced by Elliott Cumberland in UK [9]. Figure 13.2 shows a schematic diagram of the system, and Fig. 13.3 reproduces an advertisement dating from 1915. Possibly, this technique was applied to protect steam engines on ships such as the *Titanic*, in addition to steam plants and locomotives. It was used by the British Army during World War I. The justification for this new system was that zinc anodes were rapidly becoming ineffective, due to the formation of scale necessitating frequent replacements.

13.3.4 Pipelines and cables

The earliest use of cathodic protection for buried water, gas or oil transmission pipelines was at the end of the 1920s in the USA. Some gas distribution lines and a very few water distribution lines were protected only from the late 1940s. Windmills were used with limited success for feeding ICCP stations before the use of rectifiers. Before World War II, ICCP using resistor rectifiers was applied on pipe-type cables. In the 1930s, the Illinois Bell Telephone Co. protected bare lead-sheathed cables with ICCP using CuO_2 rectifiers.



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The Cumberland

ELECTROLYTIC SYSTEM

WHICH PERMANENTLY PREVENTS CORROSION & SCALE.

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P. & O.,
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Elder, Dempster,
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and other
Important Fleets
for Preventing
Corrosion & Scale
in Boilers and
Condensers.

Installed in
The Steam
Plant of Messrs.
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CONSULTATIONS & DEMONSTRATIONS BY APPOINTMENT.

An Interesting Report.

A. G. JONES & Co., Ltd.
LEATHER WORKS.
SLACK LANE,
DERBY.

THE CUMBERLAND ENGINEERING Co.,
LONDON, E.C.

December 17th, 1915.

Dear Sirs,

Re THE CUMBERLAND ELECTROLYTIC PROCESS.

With regard to the Plant at these Works, consisting of 5 Boilers and 1 Green's Economiser, we are pleased to inform you that your Process which was installed thereon on January 20th, 1915, has proved a great success.

It has removed all scale and prevented corrosion and enabled us to run our plant continuously; it has also obviated the use of the chipping hammer. The Motor Generator has given no trouble whatever.

We will have pleasure in personally recommending the adoption of this process to prospective users.

Yours truly, A. PRESTON JONES, *Chairman.*

ESPECIALLY APPLICABLE TO LOCOMOTIVES.

THE CUMBERLAND ENGINEERING Co.,
LONDON. ***6, Lloyds Avenue, E.C.***
Tel. No. 7455 AVENUE. Telegrams: CUMPROMIT, FEN., LONDON.

13.3 Advertisement for the ‘Cumberland electrolytic system’

In the former USSR, the first pilot cathodic protection system was tested on an oil pipeline near Baku in 1931. Another one coupled with stray current drainage was tested in 1946 on a Baku-Bat’umi pipeline. However, industrial use started only in 1949–1951 on gas pipelines (Dachava-Kiev and Saratov-Moscow).

Cathodic protection has been developed in many countries as a complement to the use of the method of ‘polarised drainage’ of stray currents, which was introduced a few years before for mitigating the severe corrosion that occurred on buried pipelines when DC electric railways were implemented. These methods were developed in countries where no restrictive regulations existed in this sector. In addition to the USA and USSR, Japan, Australia and, in western Europe, Belgium and Italy may be mentioned. In Belgium, Distrigaz studied this method (called ‘electroprotection’) from 1930 and tested it from 1934, mainly for fighting corrosion by stray currents, frequent in these countries, in addition to polarised drainage, which has been widely used since this date. In 1947, cathodic protection was applied to the 500 km of pipelines that were then operated by Distrigaz [10]. In France, a regulation dated 30 April 1935 slowed down the implementation of these techniques: clause 104 prohibited electrical connection between rails and metallic structures buried in the soil, and clause 133 prohibited the use of soil as a part of an electrical distribution network [11]. Although a topic of discussion in the late 1930s, cathodic protection using impressed current was not introduced until 1946, by Régie Autonome des Pétroles (RAP, ancestor of the Total group) for its gas network in south-west France, with the assistance of Distrigaz specialists [12,13]. Pipelines, laid since 1942, had suffered from premature corrosion due to DC stray currents produced by the electric railway connecting Toulouse and Bayonne. At the same time, Gaz de France, with M. Maurin, implemented studies of electrochemical methods for the prediction and mitigation of corrosion of buried pipelines. This led to the installation of magnesium anodes on some parts of a 4.1-km-long gas pipeline connecting Gennevilliers to Saint-Ouen in 1946 [14,15].

In fact, actual industrial applications of cathodic protection relate to the development of techniques during World War II, e.g. the first rectifiers using semiconductors and the development of magnesium anodes.

13.3.5 Offshore

Offshore, cathodic protection using sacrificial anodes was first applied in Lake Maracaibo (Venezuela) before World War II. ICCP was applied on a marine sub-sea water pipeline between Miami and Keywest, Florida, in 1935, using old automotive engine blocks as anodes. A larger application of offshore cathodic protection took place in the Gulf of Mexico from the late 1940s, using frequently replaced suspended magnesium anodes.

13.3.6 The protection criteria

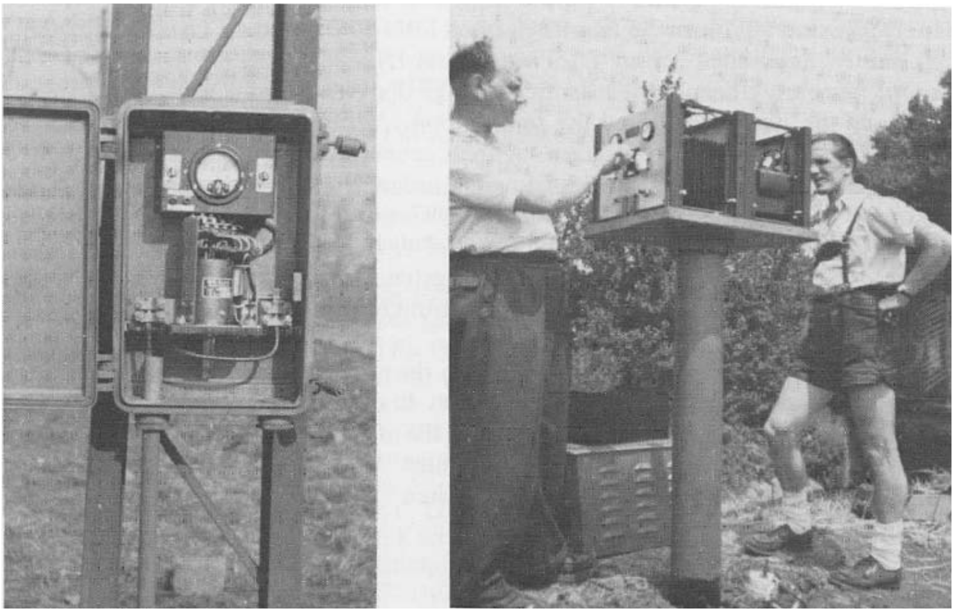
The basic protection criterion (– 0.85 V/ saturated $Cu/CuSO_4$) established by R. J. Kuhn in 1933 for buried pipelines [16] was theoretically interpreted independently by T. P. Hoar in 1937 [17] and by R. B. Mears and R. H. Brown in 1938 [18]. W. J. Schwerdtfeger confirmed the basic criterion for cathodic protection by laboratory tests in soils in 1951 [19] and in sea water in 1958 [20]. In 1952, Marcel Pourbaix and René de Brouwer wrote for the Belgian Technical Committee on Cathodic protection (CT4):

> Cathodic protection has developed on water, gas and petroleum buried pipelines since 1933. Now, these installations have a perfect effectiveness which can be easily verified, partly due to a better knowledge of the scientific basis of electrochemical behaviour of iron and steels. Cathodic protection has a large future in a number of other cases and complementary studies should be carried out [21].

13.4 Fifty years ago in Europe and all over the world

13.4.1 In Europe

When the EFC was created in 1955, cathodic protection existed but was only used for a few applications in Europe. Cathodic protection was still in its infancy. In those times, cathodic protection was often considered mysterious by non-specialists. Demystification took place during the 1960s, e.g. through corrosion societies and handbooks [7,22–27]. Applications in western Europe were, in practice, limited to a



13.4 One of the first rectifiers used by Ruhrgas in Germany for cathodic protection in 1952

few buried pipelines and jetties in some countries (the UK, France, Germany, and Belgium).

However, the actual development of cathodic protection for buried pipelines took place a little later, when refineries and transportation of natural gas and petroleum liquids developed. In 1955, only 1000 km in total of gas main pipelines existed in France, Germany and Italy. The number has now increased to about 300 000 km! In Germany, the first cathodic protection system was installed in 1952 and the first stray current drainage in 1953. A picture showing the first type of cathodic protection station using rectifiers is given in Fig. 13.4 [23].

Ruhrgas began applying cathodic protection systematically from 1958. Only 3000 km of its network has not been protected from the beginning. In the UK and the British Commonwealth, cathodic protection also became a recognised industrial process during the 1950s. As examples of early projects, Rosneath and Harwich jetties were cathodically protected by ICCP using suspended high Si–Fe anodes. Other jetties were protected in the 1960s in the UK, Kenya, and Australia. In Romania, a technical group for application of cathodic protection was founded in 1954 at the Institute of Petroleum Research (ICEP). Other groups were created afterwards for water and gas applications in Bucharest. The first cathodic protection project using zinc anodes for a desalination tank at Gura Ocnitei in Romania was launched in 1955 by Professor Radovici. Suppliers of zinc and high-Si–Fe anodes and of electrical power sources existed at that time.

In the former USSR, practically all of the major pipelines became equipped with cathodic protection only from the 1960s. Today, Gazprom operates 150 000 km of gas main pipelines, all under cathodic protection.

For marine applications, there was some, rare, use of anodes on warships and possibly some cargo ships in Europe. Offshore, no oil and gas production had started in 1955 in the North Sea, or in other places such as the Adriatic Sea or Africa. The development of these fields started in the late 1960s, but boomed mainly from the end of the 1970s. Offshore cathodic protection started in the Caspian Sea in the 1950s.

13.4.2 In other areas of the world

The applications of cathodic protection in 1955 were most advanced in the USA. Cathodic protection of gas and petroleum liquid main transmission pipelines was becoming common in order to stop the corrosion leaks that occurred with the use of coatings after World War II. However, the major increase in the use of cathodic protection on gas and liquid petroleum equipment occurred in the early 1970s, due to the Department of Transportation (DOT) rules on pipeline safety, 49CFR Part 192 (gas) and Part 195 (liquids). There was some use of cathodic protection on ships (mainly in the US Navy), but it only became extensive around 1960. ICCP was used on some wharf foundations in large ports such as New York and Boston. Offshore cathodic protection was systematic in the Gulf of Mexico (typically, suspended magnesium anodes, replaced every 2 years), but anode bracelets for the protection of sub-sea pipelines did not exist.

Other structures in contact with soil had some cathodic protection: examples included underground steel tanks, production and storage wells (with surface groundbeds), some underground piping in generating plants and industrial plants, and bare lead-sheathed cables. Many elevated water storage tanks were internally protected by ICCP, and aluminium anodes were replaced every 8 months. Some use was made of magnesium anodes in swimming pools, and heat exchanger water boxes (mainly condensers in generating plants). Only one case concerning the protection of steel in concrete is quoted: snow-melting piping embedded in concrete sidewalks is quoted.

In South Africa, the Rand Water supply company network experienced increased corrosion leaks after electrification of the Durban–Johannesburg railway line in 1938, but cathodic protection was not installed until the early 1960s. Its first use was through the installation of magnesium anodes for protecting Municipal Johannesburg gas lines in the 1950s.

13.4.3 Criteria and measurement techniques

In 1955, cathodic protection criteria, as established by a Joint Committee in the UK, were a protection level at – 0.850 V/Cu–$CuSO_4$ in aerobic conditions and at – 0.950 V/Cu–$CuSO_4$ in anaerobic conditions. All potentials were measured in 'ON conditions' (with the applied cathodic protection current), and no attempt was made to take into account and eventually correct the IR drop error in the electrolyte. The potential was limited to – 2 V in order to prevent coating disbondment. A maximum positive shift of 20 mV due to electrical interaction was allowed.

The best multi-meters used were, of course, of the analogue type, and had an internal resistance of 150 000 Ω/V. This necessitated the establishment of correction factors based on readings with two scales. The only survey method allowing detection of coating defects on buried pipelines was the Pearson method, used in many countries, such as the USA, UK and USSR since the 1950s.

13.5 Technical developments since 1955

13.5.1 Improvements with galvanic anodes

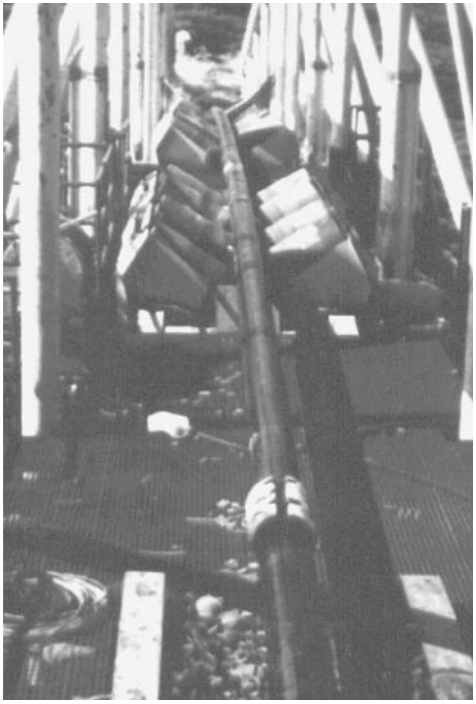
Laboratory studies carried out by the US Navy and in Europe from the 1940s demonstrated the importance of the purity of zinc for its long-term performance, leading to the development of specific zinc alloys for cathodic protection in sea water from 1955 to 1960. Aluminium anodes for galvanic cathodic protection progressively replaced magnesium and zinc in sea water, greatly reducing the costs. The main steps in the development of such anodes may be summarised as follows:

- studies on Al–Zn from 1945
- development of Al–Zn–Hg anodes in the USA (1956) and France (1959)
- widespread introduction of aluminium anodes in the late 1960s
- replacement of Al–Zn–Hg by Al–Zn–In anodes from the 1970s

Anodes were progressively installed on all kinds of ships, and on buoys, etc. The first type of anode bracelet was installed to protect sea-lines in the Gulf of Mexico in 1957, using zinc alloy in a segmented design (individual hull-type anodes welded onto bracelets through their flat cores). In 1969, the first anode bracelet design using two cast half-shells was installed in the North Sea for the first time, using zinc (Fig. 13.5). Later, Al–Zn–In alloys progressively replaced zinc, initially for high-temperature applications.

13.5.2 Improvements with impressed current systems

For ICCP anodes, the main developments have been as follows:



13.5 Half-shell type of zinc anode bracelet installed in the North Sea in the 1980s

- Scrap steel (too quickly consumed) and graphite (too brittle) started to be progressively replaced by high-silicon cast iron anodes in 1955.
- Lead alloys were introduced in 1965 for marine applications.
- 'Inert' platinised titanium anodes, first developed for chlorine fabrication, were introduced in 1966 for sea water applications of ICCP.
- Mixed metal oxide (MMO)-coated titanium anodes were introduced from 1980, mainly for applications in soil.
- Deep anode groundbeds have become popular since the 1960s, mainly in the USA to begin with.

In 1955, the current output of rectifiers was manually controlled in a stepwise fashion. Continuous control has been in common use from 1970. CuO_2 semiconductors were replaced by selenium and finally by silicon semiconductors. Air-cooled transformer–rectifiers (T/Rs) have generally replaced oil-cooled ones in the last 10 years. Lightweight, entirely solid-state T/Rs are now in common use. Automatic cathodic protection stations (controlled structure potential) have progressively been introduced when necessary (e.g. in the presence of stray currents) since the 1980s. Solar cells, considered to have no future for cathodic protection in 1969, are now being used with success for some specific applications (Fig. 13.6).

Corrosion risks related to AC interference have been considered since 1975 in Germany, and the required mitigation measures have had a major impact on corrosion protection and cathodic protection of pipelines.

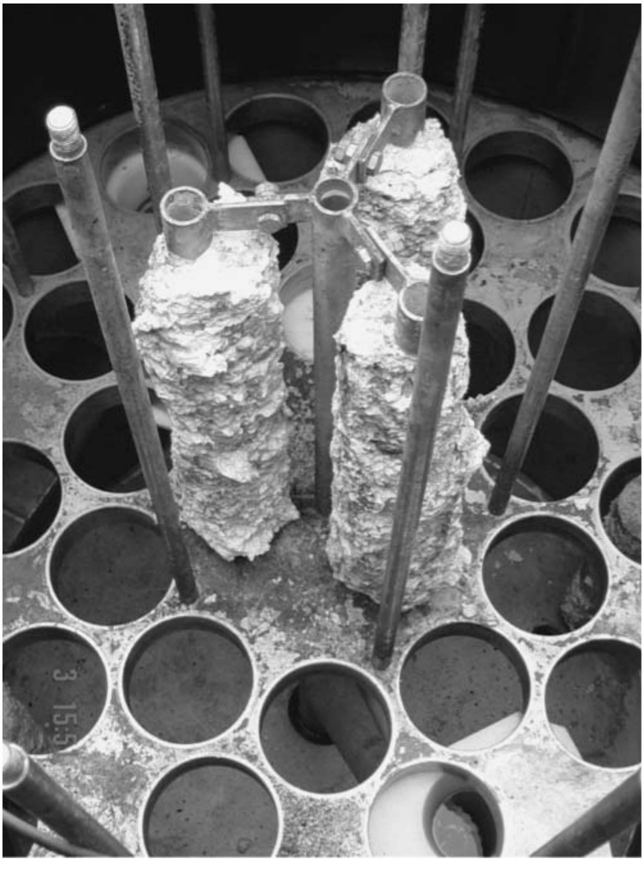
13.5.3 Newer applications of cathodic protection

The use of cathodic protection for protecting structures other than pipelines developed progressively, sometimes due to new regulations. This was the case for tanks in

13.6 Using photovoltaic solar cells in the 1980s (France) the USA in 1988, after the issue of EPA 40CFR Part 180. Cathodic protection of the external side of above-ground tanks became common in the late 1970s. The use of under-tank anode systems began in the early 1990s, for improving the effectiveness of the protection, which is often difficult to achieve, due to interference with earthing networks. Protection of spheres and cylinders installed underground for storing liquefied petroleum gas and other dangerous fluids is a difficult task that has only recently been achieved under favourable conditions.

Cathodic protection of the interiors of various kinds of apparatus has developed progressively since 1965 in the USA. In addition to water tanks, this is very common now for heat exchangers and condenser water boxes (e.g. from the late 1970s in South Africa) or sea water filters (Fig. 13.7). The Total company has systematically installed sacrificial anodes in the oil/gas/water separators in addition to coatings for about 10 years now.

Applications for protecting steel embedded in concrete (including the air-exposed zone) started in the USA and are progressing now in many regions. The US Federal Highway Agency now considers cathodic protection as the only way to prevent corrosion in the case of chloride contamination. Cathodic protection in concrete is now becoming common in Europe, including for the rehabilitation of buildings



13.7 Aluminium anodes protecting the inside of a stainless steel sea water filter

13.8 Cathodic protection of the aerial zone of a concrete structure

(The Netherlands). Alternative electrochemical methods, such as chloride extraction or re-alkalisation, are still at the experimental stage. The first systems used flat high-silicon cast iron anodes embedded in conductive asphalt. Now, platinised titanium wires or MMO mesh are laid over concrete and covered with a bearing surface (Fig. 13.8). Alternatively, sprayed zinc or zinc sheets constitute common solutions.

13.5.4 Design

Current needs have been progressively optimised by feedback from experience, together with better engineering methods, including the help of computers for design calculations or cathodic protection modelling from the 1980s.

During the 1970s, design calculations that were insufficiently accurate caused under-protection problems for some North Sea offshore structures. Modulation with time of the protective current density for bare steel (initial, mean and final values) has led to more optimal systems and has been introduced into standards.

The design current needed to protect pipelines has been drastically decreased by the use of plastic coatings (fusion-bonded epoxy, polyethylene, polypropylene) since the 1970s. Typically, the size of on-land cathodic protection stations was reduced from 15 A in 1975 to 5 A in 1995, still with a high margin of conservatism. The distance between cathodic protection stations has been increased correspondingly. The same approach became especially important offshore when steels sensitive to hydrogen-induced stress cracking, such as supermartensitic 13% Cr steels, were introduced to transport non-inhibited corrosive fluids offshore; avoiding anode attachments prevents the major cracking risks.

13.5.5 Monitoring and measurement methods

Offshore monitoring systems have been introduced to follow up the level of protection, the behaviour of sacrificial anodes and their current output (for assessing residual life), and the applied cathodic current density. Recording of potential at given locations on a platform together with the current output of some ‘monitored anodes’ throughout the life of the structure is very valuable to appreciate better the behaviour of the cathodic protection system and contribute to the optimisation of methods and hypotheses. Examination of structures after recovery is also valuable.

High-impedance (several MΩ) lightweight accurate digital multi-meters were introduced from the 1970s. Data loggers allowing convenient printouts are now in common use.

Specialists have paid attention to the IR drop error due to current flow in the ground since the 1960s (USSR) and more generally since the mid-1970s. Precise ‘ON/OFF measurements’ allowed by the use of accurate synchronous interrupters became common in the 1980s.

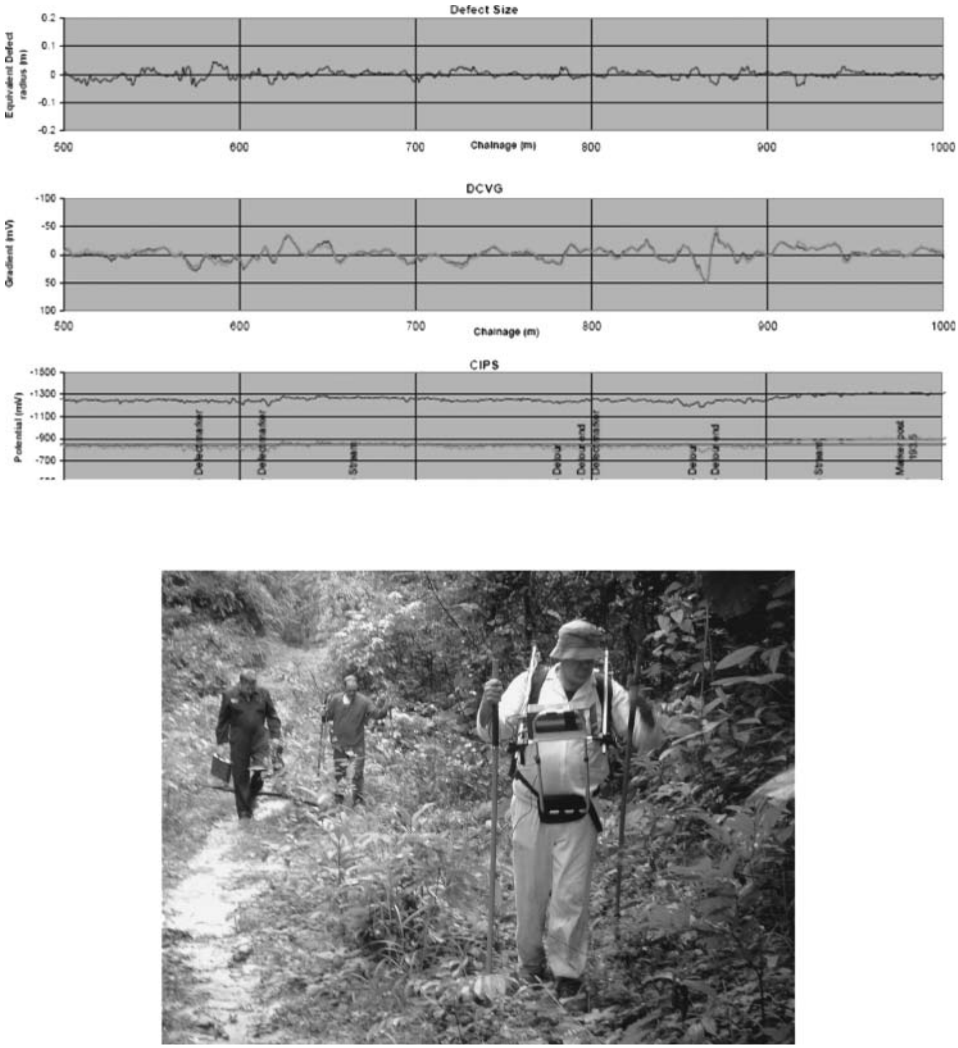
Introduced in the 1990s, remote monitoring and control are becoming more common for long pipelines. Three hundred kilometres (out of over 49 000 km) were remotely monitored in the Czech Republic in 1997. This approach is especially advanced in Italy today.

In order to solve problems of residual errors occurring with conventional ON/OFF measurements due to stray currents or complex networks, coupons allowing local ON/OFF measurements on ‘artificial defects’ were introduced from the early 1990s (in Russia, the USA, Europe, and South Africa). Electrical resistance probes are still seldom used. The use of ‘intensive measurement methods’ along pipeline routes began from the 1960s in USSR. Close interval potential surveys (CIPS) appeared in the UK in the mid-1970s and were introduced, for instance, in South Africa in 1983 but were not widely used then. Direct current voltage gradient (DCVG), developed in Europe (e.g. the UK and Germany) and Australia during the 1970s/1980s and matured in the 1990s, are now becoming usual everywhere, together with other methods such as CIPS, alternating current voltage gradient, and Pearson or electromagnetic attenuation. However, their adoption remains slow because their application is often time-consuming and difficult, and hence expensive, and only a small percentage of pipeline networks are generally inspected with this method, except in some countries such as Russia and the USA. In the USA, there is extensive use of these methods because of the integrity rules issued by DOT in 2001, leading to the external corrosion direct assessment methodology established by NACE International. An Integrated CIPS/recorded DCVG method has been developed in the UK and South Africa since 2001 to improve the intensive measurements (Fig. 13.9).

13.6 Progress in standardisation

The first actions aimed at defining a common approach to cathodic protection were originated by the Electrochemical Society and NACE symposia held in 1949. Subsequently, developments of the first standards in Europe and USA occurred in parallel. The first pre-normative document (‘Cathodic protection of buried structures’) was issued in the UK in 1957 by the Joint Committee for Co-ordination of the Cathodic Protection of Buried Structures, created in 1953. The first standard was the ‘Cathodic protection Code of Practice’ (BS CP 1021), issued in 1973, and replaced by the full status British Standard BS 7361 – Part 1 in 1991.

Other official standards have been independently and progressively issued by some European countries:



13.9 Integrated CIPS/recorded DCVG method

- In Romania, regulations were issued in 1965 on cathodic protection of buried metallic structures (revised in 1976 and 1995), followed by the 11 parts of the STAS 7335 standard issued between 1974 and 1988.
- In Germany, DVGW (the Gas and Water Association) issued its first standard in 1971, and DIN 30676 was issued in 1986.
- In Russia, GOST 9015-74 on corrosion prevention of buried structures was issued in 1974, complemented by GOST 25812-84 in 1984 for application to transmission pipelines.
- In The Netherlands, NPR 6912 on cathodic protection was issued by NEN in 1979.
- In Norway, DNV issued the first Recommended Practice (DNV RP B401) for cathodic protection design of offshore structures in 1986. A second edition was

issued in 1993 and a new one in 2005 (with a separate document for galvanic cathodic protection of offshore pipelines, DNV RP F 103, in 2003).
- In Italy, a series of UNI standards for cathodic protection of buried structures was issued from 1990 to 1993.
- In France, AFNOR issued a series of NF-A05 standards on the same topics from 1991 to 1995.

The Technical Committee CEN TC262 devoted to 'Corrosion protection of metallic structures' of the European Committee for Standardisation (CEN) created in 1990 the Sub-Committee SC2 specific to cathodic protection. Owing to the importance of the work carried out in this SC2, it was separated in 1994 and became the CEN TC219 (Secretariat provided by BSI). Ten years later, a series of EN standards (to replace existing standards in all member countries of CEN) has been issued, beginning in 2000, and more are still in preparation:

- EN 12473 (2000): General principles of cathodic protection in sea water
- EN 12474 (2001): Cathodic protection for submarine pipelines
- EN 12495 (2000): Cathodic protection for fixed steel offshore structures
- EN 12499 (2003): Internal cathodic protection of metallic structures
- EN 12696 (2000): Cathodic protection of steel in concrete
- EN 12954 (2001): Cathodic protection of buried or immersed metallic structures – General principles and application of pipelines
- EN 13174 (2001): Cathodic protection for harbour installations
- EN 13173 (2001): Cathodic protection for steel offshore floating structures
- EN 13509 (2003): Cathodic protection measurement techniques
- EN 13636 (2004): Cathodic protection of buried metallic tanks and related piping
- EN 14505 (2005): Cathodic protection of complex structures
- TS 14038-1 (2004): Electrochemical realkalisation and chloride extraction treatments for reinforced concrete – Part 1: Realkalisation

In the USA, the first Recommended Practice (RP) issued by NACE in 1969 was mainly concerned with cathodic protection: RP 01-69, 'Control of external corrosion on underground or submerged metallic piping systems'. Subsequently, a series of RPs devoted to cathodic protection was issued and updated by NACE. In addition, the Steel Tank Institute issued standards on provisions for cathodic protection of buried and above-ground tanks in the 1980s, and the American Petroleum Institute also published in 1975 RP 651, 'Cathodic protection of aboveground petroleum storage tanks' for petroleum tanks (revised in 1997).

In South Africa, the Code of practice SABS 0121 was issued in 1977, and in Australia five parts of the Standard AS 2832 relating to the various applications of cathodic protection were published between 1991 and 2005.

For international standardisation, ISO TC156 devoted to corrosion created WG10 for cathodic protection a long time ago, but no standard has been issued yet. At present, some EN standards are being adopted as the basis for future ISO standards through fast-track votes. In addition, ISO TC67 (Oil & Gas Industries) published in 2000 the ISO 13623 standard devoted to design, installation, operation and maintenance of pipelines, which addresses cathodic protection. In addition, more specific standards for the cathodic protection of pipelines were issued in 2004, ISO 15589 Part 1 (onshore) and Part 2 (offshore).

13.7 The progress in certification

It became progressively obvious that third-party verification of competence of cathodic protection personnel and companies was needed to ensure the quality of design, implementation and control of cathodic protection systems. In the USA, NACE introduced a general Accreditation Program in corrosion in 1971. A specific Corrosion Professional Recognition Program was devoted to cathodic protection in 1987. A newer system, called the NACE CP Training and Certification Program, was put into place in 2000. Since 2004, four levels (level 1 for CP Tester, level 2 for CP Technician, level 3 for CP Technologist, and level 4 for CP Specialist) have existed, without specific application sectors.

The oldest European certification system for cathodic protection companies for buried gas or water pipes and tanks, based on evaluation by a committee of experts, has been operated since 1976 in Germany by DVGW and specified by Merkblatt GW11. Fifty companies have now been certified. In France, the Conseil Français de la Protection Cathodique (CFPC) was launched by CEFRACOR in 1996, and has been mandated since 1998 for the award of the AFAQ AFNOR Compétence mark for cathodic protection personnel in accordance with NF A05-690 and 691 (three levels, four application sectors). One hundred and sixty certificates have been awarded so far. A standard on certification of services (NF A05-800) was published in 2006. In Italy, a similar system based on the UNI 10875 standard, published in 2000, has emerged from an agreement signed in 1996 between APCE (for the technical programme and training) and CICPNP (for examinations). In the UK, an older professional assessment system operated by the Institute of Corrosion for 'Professional Members and Fellows' still exists. In addition, an Institute of Corrosion Scheme for the Certification of 'Technician Members' for Painting and Coating Inspection or Cathodic Protection was implemented in 1996, with two levels for cathodic protection technicians (no specific application sectors). In The Netherlands, an older accreditation programme for cathodic protection measurements on underground tanks has been completed by certification of cathodic protection personnel since 2001 (three levels, only for buried structures).

Following the WP16 report on 'Qualification and certification in the field of cathodic protection: Present situation and possible European scheme', issued in May 2001, the new European Standard EN 15257, 'Competence levels and certification of cathodic protection personnel' has been issued recently. It provides a 'framework' allowing independent national certification bodies to operate with demonstration of equivalence of levels through the European Multi-Lateral Agreement system, working on the basis of audits performed by the accreditation organisations. It is based on the possibility of implementing three levels of competence and four application sectors (Land, Marine, Concrete, and Interior of Apparatuses), precisely defined in EN 15257.

13.8 The future

The verification of actual effectiveness of external corrosion protection of buried pipelines has to be further improved in order to provide as closely as possible a complete and true picture of their status: improved intensive methods working with stray or telluric currents, methods for detecting coating disbondment, with or without penetration and renewal of electrolyte, with or without corrosion, optimisation of the use of coupons, etc. An EFC publication is in preparation.

Remote monitoring and control, involving the use of cellular and satellite communications, should be further developed. It is probable that no more routine surveys on site will be performed during the next 50 years.

DC stray current analysis techniques have to be developed. Criteria related to corrosion risks induced by AC stray currents have to be better defined. Coating breakdown factors used for the design of coated structures are highly over-estimated and should be better optimised on the basis of consolidated field experience, mainly offshore (for floating structures, pipelines, etc.).

Criteria for the protection of reinforcement in concrete still have to be clarified. Limits of potential have to be better defined as regards the detrimental effects of cathodic protection on sensitive materials and coatings. Wider use and engineering of better quality have to be developed for cathodic protection in certain application sectors such as the water industry, non-industrial equipment, and concrete structures. In the oil and gas industry, the quality of cathodic protection design has to be improved for some 'minor' items of equipment, such as sea water filters and separators. Cost-effective retrofitting methods have to be developed for mature offshore structures.

Standardisation should be completed as soon as possible at the ISO level, the final goal being a unique, well-proven and accepted series of standards. Certification of cathodic protection personnel has to be put fully into practice, and here, also, the final goal for ensuring worldwide equivalence of competence levels should be to achieve implementation of a unique international (ISO) scheme.

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14

Corrosion and its manifestation in automotive structures

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14.1 Introduction

The automotive industry is characterised by its major economic importance, and offers many positive and promising perspectives, in particular with the rapid progress of globalisation. The International Organisation of Motor Vehicle Manufacturers (OICA) reports some key figures [1]. Global motor vehicle production reached 66.2 million in 2004, as compared to 53 million in 1998. With a turnover of around 1.6 trillion euros, this industry is equivalent to the sixth largest economy worldwide. A very interesting statistic is the investment in research, which, at about 66 billion euros, explains why this sector also plays a key role in the level of technology in other industries.

Looking back over the past four decades, the technology changes in the automotive sector have always been governed by materials–energy–environment considerations. After the environmental issues of the 1960s leading to the implementation of the exhaust gas regulations, the 1970s were characterised by energy issues (oil crises) resulting in specific emphasis on the development of fuel efficiency technologies. In the early 1980s, cold-rolled steel sheet was still the predominant material for automotive body construction. However, the unacceptable level of failures due to corrosion [2] forced the automotive manufacturers to improve car body design, and the steel producers and chemical and pre-treatment suppliers to look intensively for solutions in order to extend the lifetime of vehicles. The huge step change was made with the introduction of galvanised steels such as hot-dip galvanised, electro-galvanised and galvannealed materials [3]. Combined with improved surface treatments, better paint systems and designs, this resulted in an increase in vehicle lifetimes, allowing guarantees of 6 years' resistance to perforation by corrosion and cosmetic corrosion to be offered.

From the1990s to the present day, environmental aspects have continued to play a major role, favouring the introduction of lightweight materials (Al, Mg, plastics) in car bodies to reduce CO_2 car emissions, and provide recyclable materials and environmentally friendly processes. In the European Union (EU), new regulations are in place banning the use of chromium (VI) from July 2007. Although chromates had been used for post-rinsing after phosphatisation, most automotive manufacturers had already changed to chromate-free post-treatment alternatives. With the large combination of materials, in particular different metals, galvanic corrosion is a threat. Also, the post-treatment and painting processes have to be adjusted to ensure acceptable corrosion protection of all structures. At the same time, lifetime guarantees, which have extended to 10–12 years during this period, are still increasing (up to 30 years for some manufacturers) without detriment to safety, aesthetics and cost.

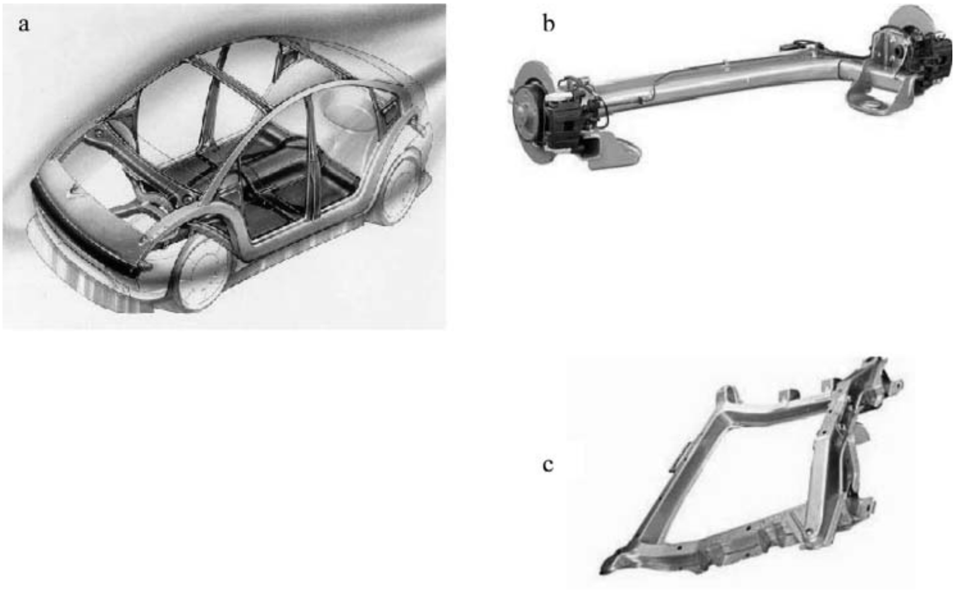
Throughout these years, durability aspects have clearly always been considered. With all these changes, including demands for longer warranties and their impact on corrosion and corrosion control, intensive research has been needed to evaluate existing solutions.

With this in mind, in 1998, Professor Hans de Wit of Corus Steel and Delft University proposed the formation of a new European Federation of Corrosion (EFC) Working Party (WP) on Automotive Corrosion. This was approved as WP17 in the following year, with Frits Blekkenhorst of Corus Steel as its first chairman. He continued in that position until 2004, when he was succeeded by Fouzia Hannour of Corus Research, Development and Technology. In this contribution, she and two colleagues from WP17, Jean-Louis Baudoin and Philippe Rolland, both of Renault Technocentre, discuss the corrosion aspects of automotive structures, where two main type of corrosion are of concern: perforation and cosmetic corrosion. Cosmetic corrosion starts at the outer surface, where scratching or stone chipping has caused local damage to the paint. In contrast, perforation starts from the inside at the most sensitive parts, such as cavities, interior hem flanges and lap joints, which favour the entrapment of salt and water. The main factors contributing to overall corrosion resistance are highlighted, namely the base material, design, fabrication processes and post-treatments (coatings). The protective measures taken to minimise damage, such as waxes and sealers, are outlined, along with information from accelerated tests and field studies.

14.2 Basic manifestations of automotive corrosion

In automotive applications, typical forms of corrosion are closely linked to the nature of the materials involved and to the design of the parts. Three systems covering these aspects are: the body-in-white (BIW), the front axle, and the sub-frame (Fig. 14.1).

The BIW represents the body parts of the car, and includes all the components that are welded or adhesively bonded (including both exterior and inner panels) before going through the painting line. The other parts of the car, such as the front axle and sub-frame, are married to the BIW at a later stage in the production line. Whereas the BIW is visible, the rear axle and the sub-frame are not normally visible. They serve only functional purposes, the sub-frame supporting the engine and the axle supporting the wheels. Because of their position in the car, these two parts are subject to aggressive corrosion conditions. Therefore, nowadays, the entire BIW is often fabricated from steel sheet that has been galvanised on both sides. Parts of the rear axle are made from cast iron, and the sub-frame can be hot-dip galvanised material, coated after assembly.



14.1 Schematic structure of a car showing: (a) the BIW; (b) the rear axle; and (c) the sub-frame

14.2.1 Cosmetic corrosion

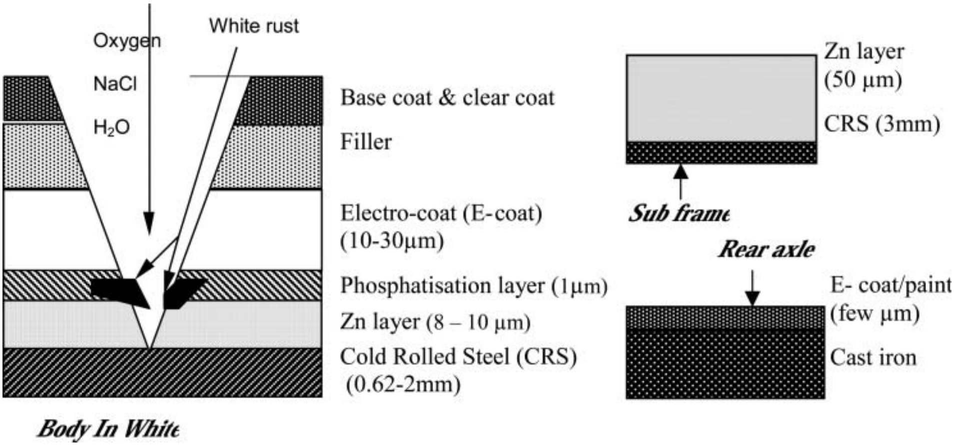
The environmental factors that cause degradation of car body panels are salt (de-icing salt, and salt from the sea in marine environments), humidity, temperature, acid rain and wet–dry cycles. Polymer protective coating systems have improved in recent decades, and the environmental factors usually have a minor, slow-acting effect on the degradation and disbondment of the paint. However, the most direct cause of corrosion initiation is physical damage to the paint by scratches, stone impacts (stone chipping) or impact by pebbles or sand, leading to cosmetic corrosion. This type of corrosion starts on the exterior surface of the car and is usually visible in its early stages. The propagation of any corrosion process depends not only on the depth of the damaged area but also on the nature of the protective system, particularly the first layer that is directly exposed to the corrosive environment.

As Fig. 14.2 illustrates, the complete protective system for the outer panels of automobiles comprises various layers, each one having a specific function. The corrosion mechanisms of painted galvanised sheets (as in the case of the BIW) have been extensively studied [4–6].

As polymer protective coatings have good barrier properties, and as long as the electrocoat layer is not damaged, there is no real corrosion issue or risk of delamination. However, as proposed by Granata [4], if water and oxygen can reach the phosphate layer by diffusion, cathodic delamination can begin. The pH increases at cathodic sites as a result of the cathodic reaction

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

and, subsequently, the phosphate layer dissolves rapidly without providing any real protection. Eventually, a blister will form. The zinc layer is consumed locally by the



14.2 Schematic representation of the coated materials used in automotive systems for the BIW, sub-frame and rear axle, showing how an impact can result in damage extending to the steel substrate of a BIW painted system (picture drawn freely after Granata [4])

anodic reaction, and the steel substrate is exposed. Zinc oxide, hydroxide or hydroxychloride produced by the dissolution of zinc migrates to the steel surface and forms a white precipitate. In real service conditions, as the whole system goes through wet–dry cycles and temperature transients, both anodic and cathodic reactions are halted, and the spread of damage is stopped. These white corrosion products are not objectionable in appearance and eventually retard dissolution of the zinc.

14.2.2 Crevice (perforation) corrosion

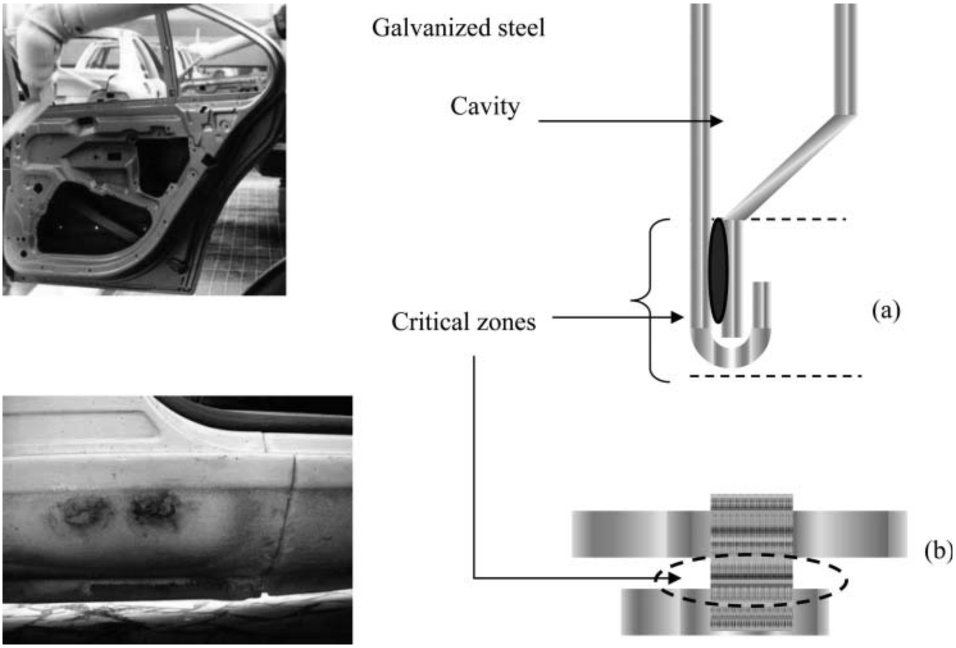
The design of a car includes many box sections and joints (welded or glued). Such geometries as hem flanges and lap joints (Fig. 14.3) favour the entrapment of debris and water from the roads.

The natural environment (acid rain containing SO_2 or NO_2, snow, ice, etc.), combined with anthropogenic factors (de-icing road salts and pollutants), can provide a very aggressive environment, to which such parts can be susceptible [6]. The composition of the mudpacks collected from cars have been studied, and they have been shown to be mainly a mixture of sodium and calcium chlorides [7].

This leads to the most damaging type of corrosion, the so-called crevice or perforation corrosion, which is usually invisible in its early stages but eventually causes failure of the part. Thus, by the time that perforation corrosion is discovered, repair is rather difficult. Therefore, it is considered to be the most important problem in automotive corrosion resistance.

This type of corrosion is associated with small volumes of stagnant solution trapped in holes. In general, the corrosion process can be divided into three or four stages, as follows.

It starts on the surface of Zn layers, where Zn is preferentially dissolved by the anodic reaction.



14.3 Door panel (before and after 6 years of corrosion exposure) showing two sensitive geometries: (a) hem flange; (b) lap joint

Then, corrosion products [ZnO and $ZnCl_2.4Zn(OH)_2$] protecting the underlying steel are formed by reactions between ZnO and H_2O and Zn ions and chlorides, following the path:

$$Zn^{2+} + 4ZnO + 4H_2O + 2\,Cl^- \rightarrow ZnCl_2.4Zn(OH)_2$$

$$Zn^{2+} + 8H_2O + 2Cl^- \rightarrow ZnCl_2.4Zn(OH)_2 + 4H_2$$

In the final stage, the steel substrate is consumed from the inside to the outside of the panel, according to the redox reaction in wet conditions:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

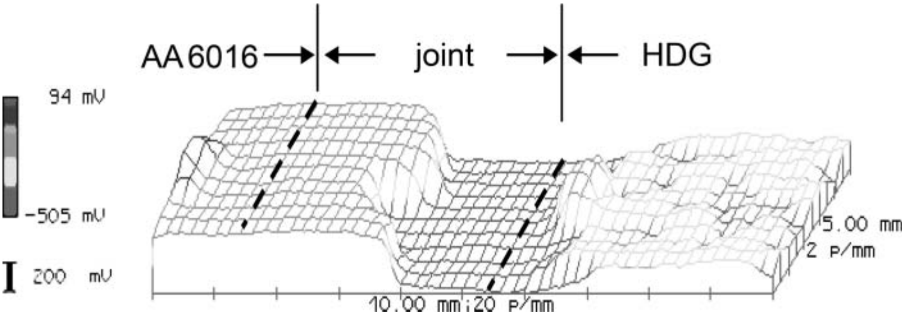
$$Fe^{2+} + 2FeOOH + 2e^- \rightarrow Fe_3O_4 + H_2$$

JFE steel carried out research looking at the effect of the various types of galvanised steel on perforation corrosion and the associated mechanisms [8]. The study was based on recovered automobile hem flanges using zinc and zinc alloy metallic coatings and also on a test simulating a lap joint, which was packed in advance with iron corrosion products, Zn and $ZnCl_2.4Zn(OH)_2$. Furthermore, measurement of the perforation depth and analysis of the corrosion products were undertaken after 5 and 8 years of use. The results showed clearly that the corrosion of the steel substrate and therefore the perforation is controlled by the existence of the zinc corrosion products reported earlier. A mechanism was proposed based on characterisation of the corrosion products obtained after 20 corrosion test cycles in the crevice of a lapped steel sheet. If lapped portions were initially packed with ZnO or $ZnCl_2.4Zn(OH)_2$, no α-FeOOH, β-FeOOH or γ-FeOOH was found. According to the authors, these zinc corrosion products inhibit the redox reaction of iron rust products and therefore prevent the steel from corroding. Another study [9] characterised the corrosion products on each area of hem flanges pre-coated with zinc, and showed that after 8 years of use, the cavity was the initiation site for corrosion, as it had no trace of zinc corrosion products and the most stable α-FeOOH was present.

14.2.3 Filiform and galvanic corrosion

With the strong push for weight reduction, fuel efficiency and environmental friendliness, lighter materials such as aluminium are receiving increased interest as alternative materials for the BIW. Today's European car contains an average of 100 kg of aluminium. One growth area for the application of aluminium is within the vehicle structure. Aluminium allows an optimised BIW to weigh approximately 40% less than a conventional steel equivalent. However, using aluminium results in higher cost, so the use of aluminium for the primary body structure has been employed for only a few lower-volume and higher-cost vehicles. Future cars will be built using multi-material lightweight design, and the use of aluminium in the BIW has started with bonnets, wings and doors. For automotive body panels, much effort has been made in improving formability during stamping and in increasing the strength of the formed parts after painting. These attempts have been partly limited by fear of higher corrosion susceptibility when copper is used as a strength-improving element. In Europe and Japan, this has led to the acceptance of the alloy AA6016. However, the specification for copper content in Japan is far less ($<0.01\%$) than in Europe ($<0.2\%$). US manufacturers have less rigorous demands, and use AA6111 (up to 0.9% Cu). Some authors [10] have investigated the influence of copper on filiform corrosion as a cosmetic corrosion issue in painted aluminium on various alloys: AA6016 with different copper contents ($<0.01\%$ and 0.07% Cu) and AA6111 (0.7% Cu). It was shown that the alloy with the highest copper content was more susceptible to filiform corrosion in the various laboratory tests used. It could be concluded that the materials supplied in Europe, which usually contain less than 0.2% Cu, can be used safely.

If aluminium and steel are in electrical contact, it does increase the susceptibility to galvanic corrosion, which depends on the electrochemical properties of the metals to be joined and the joint itself. Authors [11] recently reported an investigation on aluminium–hot-dip galvanised steel combinations joined by laser welding (Fig. 14.4). AA6016 Al alloy was studied using a scanning Kelvin probe on bare, zinc phosphated and electrocoated specimens. In addition, for comparison, panels were subjected to accelerated cyclic corrosion tests, including the Hoogovens cyclic test and the VDA 621-415 test of the German Association of the Automotive Industry. The results showed that the microstructure and composition changes resulting from such joint configurations during the brazing process significantly influence the corrosion properties of the joint. Kelvin probe potential mapping (Fig. 14.4) showed that corrosion and coating delamination start locally at the interface between the galvanised steel and the joint. However, relatively long exposures were required during accelerated testing (i.e. 10 weeks for VDA) to achieve detectable corrosion and coating delamination at the joint. This indicates that the galvanic coupling effect is only moderate and can be controlled with an appropriate coating system. In conclusion, from a corrosion point of view, AA6016/galvanised steel laser-brazed joints certainly appear to be applicable for car bodies (i.e. roof-type applications).



14.4 Potential map of AA 6016/HDG laser-brazed joint, after exposure for 2 days in the atmospheric Kelvin probe chamber

14.3 Current corrosion protection solutions

14.3.1 Galvanising and painting application

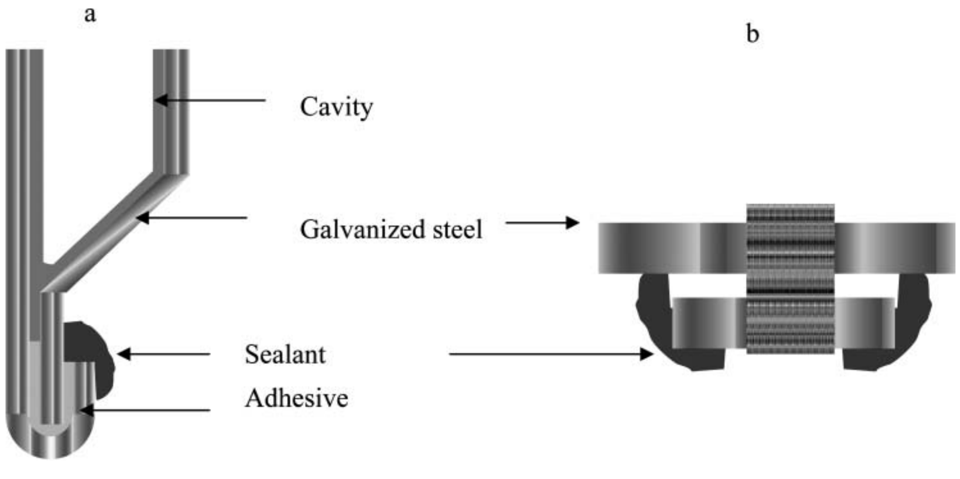
Since the beginning of the 1980s, car makers have extended the lifetime warranties of vehicles, thanks to the increased use of galvanised material. Depending on the car application, the preference is for hot-dip galvanised, electro-galvanised, galvannealed (Zn–Fe alloy) or Zn–Ni alloy-coated sheet [12]. The requirements, especially for body panels, are high corrosion resistance, good formability, defect-free coating surface, surface roughness, good weldability and paintability. All these requirements can be met by hot-dip galvanised steel in a cost-effective manner, and the trends in Europe and the USA show an increase in consumption.

From the corrosion standpoint, galvannealed material offers better cosmetic and perforation corrosion performance over galvanised sheet. This is indirectly due to the excellent adhesion between the Zn–Fe metallic coating and the electrocoat layer. In [13], after light microscopic investigations on metallographic cross-sections, it was shown that at high strip temperature the Γ-layer and the mixture layer (Γ_1 and δ) are very irregular and are interrupted in many places by craters, allowing better penetration of the electrocoating primer. However, the corrosion properties are still determined by the coating thickness and the type of metallic coating (Zn, Zn–Ni, Zn–Mg, Zn–Fe).

After assembly, the BIW is further processed in the painting line, in which each step (coating layer) has a specific function. The first layers (Fig. 14.2), namely phosphating and electrocoating, are crucial for the overall corrosion behaviour. After alkaline degreasing, the phosphate coating is nowadays applied by a mixed spray-dipping process and is a ternary system: Zn–Mn–Ni. The phosphate coating weight, the crystal shape, the crystal size and the coverage are the determining factors: the larger the amount of crystal, the better the corrosion resistance. This intermediate phosphate layer has some corrosion resistance properties, but these are rather limited, as it is a pure inorganic layer with a low thickness (3 µm). In fact, its role is mainly to enable the adhesion of the electrocoat, which plays a key role in the corrosion resistance of the whole system. Electrophoretic (cataphoretic) deposition is a process in which positively charged polymer particles are deposited from a water suspension in a tank containing the entire BIW, negatively charged. The electrocoat is organic-based and consists of a mixture of binder, pigments and additives. The process takes place at voltages of 200–400 V and at current densities of 10–100 A/m^2, and is optimised in order to reduce pinholes or cratering. For the final paint appearance, top coats are applied for chemical, scratch and UV resistance, whereas the filler or primer is applied to level the electrocoat and ensure resistance to stone chipping.

14.3.2 Addition of wax or sealant/use of pre-coated sheets

Many sections of the automobile contain joints and hem flanges. The penetration of electrocoating in these areas is rather difficult and not optimal, as the electrocoating is deposited under an electric field. These areas act as a Faraday cage, preventing deposition of the electrocoat. The most common solutions consist of the addition of wax in the cavity and the use of an appropriate sealant to prevent the entry of water and contaminants such as mud or road debris. Sealants are resins (epoxy or PVC) and act as a barrier by excluding the corrosive environment (hydrophobic). Adhesives are often added in hem flanges to fill the gap, as shown in Fig. 14.5. Wax and sealants are applied by hand or with robots. The Swedish Corrosion Institute has, in an extensive investigation [14], studied the corrosion resistance in cavities and crevices of 18 selected car models from 1989 and 1992. From a total of 845 cars damaged in collisions, parts from doors, bonnets, boot lids, rear wings/wheel arches and bottom sills were sawn out and examined in order to investigate the corrosion effects after 4 and 7 years of use. It was concluded that good penetration of both electrocoat primer and anti-rust agent as well as an effective application of adhesives help to prevent corrosion for periods in excess of 4 years. This illustrates that design plays a major role, and a guideline with suitable geometries has been proposed as a way to improve corrosion resistance, in particular by optimisation of the electrocoat penetration but also by preventing water and mud entrapment [15]. As a result, the addition of wax, sealant and adhesive has allowed major improvement in the lifetime of vehicles, and is now common practice. In the process, these solutions are added in various steps: the adhesive before the electrocoat, the sealant usually after the electrocoat, and the wax after the full paint system.



14.5 (a) Hem flange protected with electrocoating wax, sealant and adhesive. (b) Lap joint with confined areas sealed

Another solution has been the use of sheet pre-coated with organics. However, it should be noted that the organic coating that is used is not actually a substitute for post-painting, as is principally the case in the construction and appliance industries, but is added for extra corrosion protection. The one important advantage is the reduced necessity for secondary corrosion protection with sealants or wax. As a result, it is sometimes referred to as a 'pre-sealant'. However, as yet, it is not used as a pre-primer or a pre-painted material, since it cannot replace either the electrocoat or all four coats in the traditional automotive paint system. Organic pre-sealants are thin, at around 3–4 μm. They are based on modified epoxy, and contain zinc dust particles for weldability, plus various silicates. The weldability is a major advantage, since most steel parts of the traditional motor vehicle body are joined by welding.

This enables the pre-coated sheet to be used beyond hang-on panels, including areas where its special corrosion protection is far more important, such as inside doors. However, the film thickness has to be carefully controlled to give a good corrosion barrier coating while remaining thin enough to give good weldability. Two paint manufacturers have developed these products: Henkel and PPG, under the brand names Granocoat and Bonazinc respectively. Over the period 1996–2001, organically coated sheet produced on European paint lines for the automotive industry has grown at a cumulative average growth rate of 30.4% per annum. However, until now, this growth has been largely attributable to one company, the Mercedes-Benz division of DaimlerChrysler, and, to a lesser extent, to Volkswagen and Renault. Renault protects areas subject to severe aggression by using mastic and wax (Table 14.1), pre-coated steel sheets being reserved for areas where the former solution is not applicable, due to design.

14.4 Field studies, accelerated corrosion testing and fundamental corrosion studies

Corrosion testing is crucial for material evaluation, as it provides the required information for performance prediction, which assists both metal suppliers and car manufacturers in their research and development. The literature is full of tests for the automotive industry, and it is not intended to describe all of them but rather to give an indication of the fundamental information that can be extracted from them. There are various approaches. One method consists of investigating the corrosion

Table 14.1 Overview of the various corrosion manifestations in the three typical automotive parts and the current associated solutions

Part	Cosmetic	Hem flanges/Lap joints	Cut edges
BIW	0.62–2-mm CRS, Zn (10 μm each side plus electrocoat)	Wax and sealant, as the electrocoat can become very thin or non-existent (0.5–2 μm) rather than the normal 20–25 μm	High coverage of electrocoat or mastic covering the edges
Front sub-frame	2.5–3-mm CRS, Zn 50 μm, no need for electrocoat	No need for wax, Zn plays active role	Covered by Zn
Rear axle	No corrosion issues, may be painted	–	–

behaviour of cars after practical use. As already mentioned, the Swedish Corrosion Institute used this approach [14]. Material was recovered from dismantled vehicles, and the corrosion resistance in cavities and crevices of 18 selected car models from 1989 and 1992 was studied. Another method adopted by the Automotive Corrosion and Prevention Committee of the SAE (Society of Automotive Engineers) consisted of conducting biannual surveys of car bodies by examining cars in closed car parking lots for perforations, blisters and surface rust on specified parts. Each survey covered between 200 and 800 cars of all models and manufacturers, ranging in age from 5 to 8 years [16]. However, gathering the information is time-consuming and expensive. Furthermore, it cannot be used as a predictive tool to develop new materials and designs. Therefore, early on, automotive manufacturers developed methods such as on-vehicle testing, where racks with coupons are attached to vehicles and regularly inspected, proving ground testing of prototypes, outside atmospheric exposure testing and accelerated corrosion testing in the laboratory. The first accelerated test developed, still used nowadays, was the salt spray test (ASTM B117). This test gives results that are not representative of service, as it works under constant wetness, whereas, in the real world, intervals of wetness and dryness are interposed. For example, in this test, painted cold-rolled sheet (CRS) would give better performance than zinc-coated steel, obscuring the protection offered by the zinc oxide layer.

To escape from this constraint, car companies have developed accelerated cyclic tests, consisting of repeated exposure to salt solutions (immersion or spray) followed by cycles of humidity and drying periods. Within each phase, these tests define various parameters: temperature, relative humidity, time of exposure, salt composition, and frequency of cycling. As examples, some of the test conditions are given in Table 14.2: the SAE J2334 test defined by the American Society of Automotive Engineers, the German standard test VDA 621-415, and the Renault ECC1 test.

Although these tests are still undergoing improvement, they represent real conditions relatively well. However, they have been developed for cosmetic corrosion. In the case of perforation corrosion, by the mechanism reported above, the correlation is more difficult. In this case, the geometry is the major factor influencing the corrosion behaviour and, therefore, crevice coupons mimicking the hem flange of a door or other assembled parts have been developed, the SAE cell being the most widely used [17]. In general, panels are fixed together with screws and with a spacer between them before being processed using normal painting procedures (e.g. phosphating and electrocoat primer). The results obtained using these cells correlate rather well with real conditions, but give very little mechanistic information. Recently, a novel corrosion cell with a PM-IRRAS (Polarisation Modulation Infrared Reflection

Table 14.2 Examples of cyclic corrosion tests used by some automotive manufacturers

Test	Salt application conditions	Drying period	Humidity period
ECC1 (Renault)	1% NaCl, pH = 4, 35 °C, 30 min	55%, 2 h 40 min	90%, 1 h 20 min
SAE J2334 (USA)	15 min room temperature, 0.5% humidity, NaCl + 0.1% $CaCl_2$ + 0.075% $NaHCO_3$	50% humidity, 17 h 45 min, 60 °C	50%, 100% humidity, 6 h
VDA 621 415 (Germany)	5% NaCl, 24 h, 35 °C, 100% humidity	50%, 23 °C, 48 h	99% humidity, 40 °C, 32 h
Salt spray test (ASTM B-117)	5% NaCl, 35 °C, continuous spraying	None	Continuous 100% humidity, 35 °C

Absorption Spectroscopy) spectrometer combined with a video recording system during the drying periods has allowed a better understanding of the mechanisms. It has been shown that the drying process in lap joints is heterogeneous and long, and that the corrosion develops rapidly during the drying phase. Corrosion reactions start first with the formation of zinc oxide and hydroxide, and then produce a neutral or basic environment in which hydroxychloride or hydroxycarbonate, respectively, can appear. Accelerated corrosion tests, initially developed for cosmetic corrosion, have to be adapted, in particular during transition phases, which have to be controlled in a better way to simulate the degradation of lap joints [18–20].

14.5 New constraints and future developments

In today's automotive market, car manufacturers have to offer a good package with safety, comfort and warranties (good corrosion resistance), and this has also been a main driver for developments undertaken by their materials suppliers. However, in Europe, this has to be achieved with some constraints, and these solutions may need to be re-evaluated.

The first constraints are the environmental regulations for the automotive market: EU directive 2000/53/EC, better known as an end-of-life vehicle regulation, bans all heavy metals, including cadmium, chromium, mercury and lead. Hexavalent chromium in corrosion-preventive coatings had to be completely phased out by July 2007, and lead by July 2005. For the BIW, the replacement of the chrome-containing post-rinse with chrome-free alternatives has been achieved by some car manufacturers. In the case of the electro-galvanised coatings, which are widely used for nuts and bolts, new cost-effective chrome-free solutions exist, with similar performance. In the latter case, the replacement of Zn + Cr(VI) by ZnNi + Cr(III) gives excellent corrosion results. In the case of lamellar zinc coatings, a number of solutions without chromium(VI) are available, such as Geomet®, Deltaprotekt®, Magni® and Zintek®.

There is also pressure for better fuel economy to reduce CO_2 emissions, and hence a trend to reduce vehicle weight. This can be achieved by proper design, using, for example, tailor-welded blanks and hydroformed tubes and by using lighter materials such as aluminium and possibly, in the future, magnesium. Obviously, this is not without consequences for the corrosion resistance of the parts, and the use of many different materials in a car body will pose new challenges to designers to prevent galvanic corrosion.

A second constraint is the trend to provide longer lifetime warranties, which necessitate the development of technical solutions. Currently, new metallic coatings with higher corrosion resistance are also under development. In society, there is also pressure to re-use and recycle materials after the useful life of a car has ended, and in the evaluation of materials and designs, this will play an increasingly important role.

Another constraint is globalisation, at a time where steel consumption is increasing in Asia and the automotive market is growing. From a corrosion viewpoint, all solutions developed in recent decades have to be revised, and the manufacturers must consider assessing the level of corrosion severity per location and developing solutions to protect vehicles in the most severe areas of the world. A large programme involving car manufacturers and metal suppliers looking at the relative corrosivity of the natural vehicle environment on a global basis and coordinated by the Swedish Corrosion Institute is currently ongoing [21].

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Note: Page references in *italics* refer to illustrations