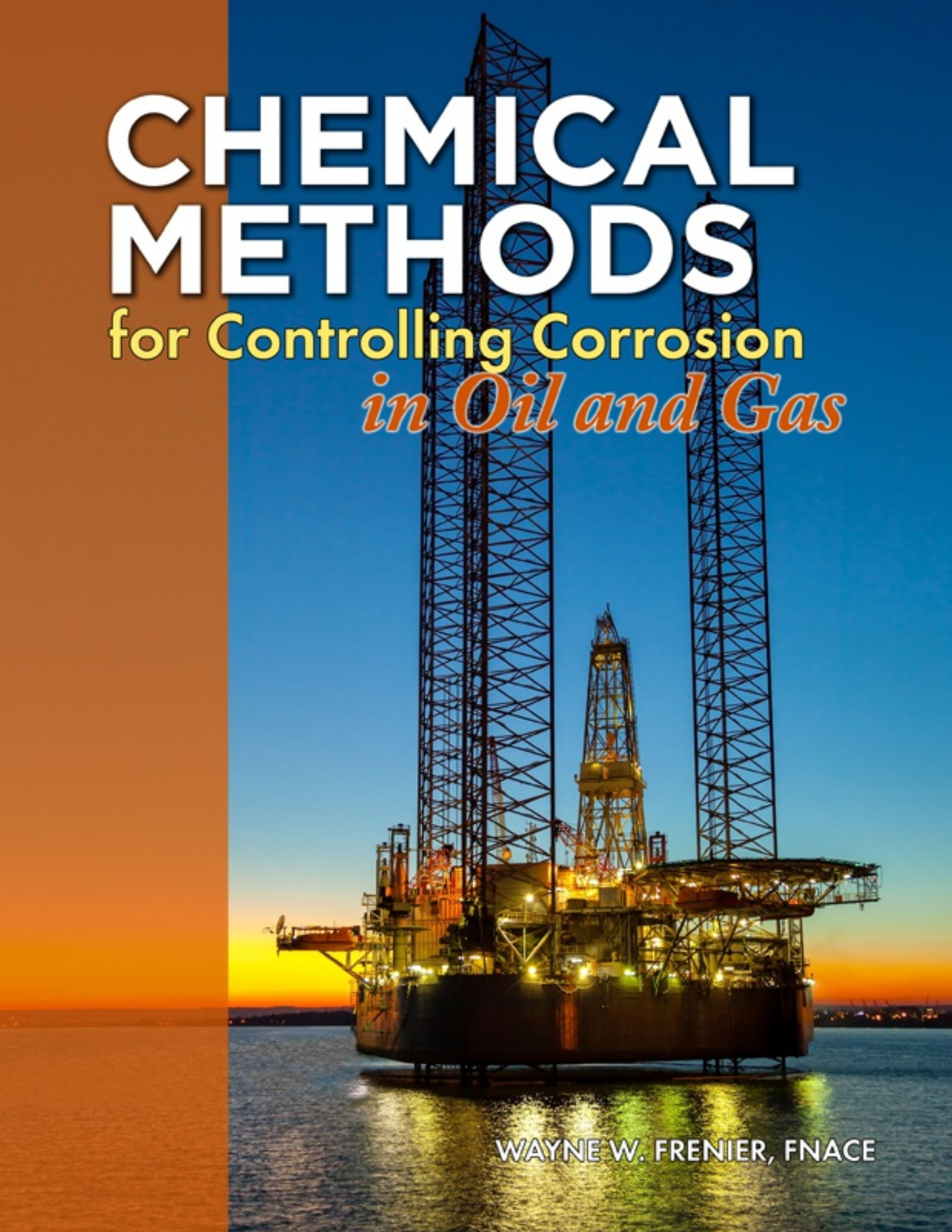
CHEMICAL METHODS

for Controlling Corrosion *in Oil and Gas*



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Chemical Methods for Controlling Corrosion in Oil and Gas

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Preface

This book gives an overview for a general technical audience of the science and technology for corrosion control using chemicals. However, since this book is specialized, some knowledge of corrosion processes (such as provided by the NACE International[1] Basic Corrosion Course) is assumed. In addition, knowledge about chemistry equivalent to an introductory college chemistry course is recommended.

This book emphasizes the basic chemical and mechanical principles for corrosion control. These subjects include surface corrosion inhibitors (CI), other chemicals like biocides and acid gas control chemicals, and application methods. A major goal is to demonstrate that similar chemical and hydraulic principles occur in each segment of the O&G environment. Thus, understanding these principles leads to an understanding of chemical corrosion control methods in the different (but connected) segments of this industry.

The introductory chapter describes the environment where damaging corrosion attacks occur and places the technical aspects of corrosion management in a perspective of the upstream and midstream oil and gas business. Subsequent chapters discuss aspects of corrosion-control requirements. Subjects include chemical mechanisms for limiting corrosion, the wide variety of corrosion-controlling chemicals in use, on-site application methods, and health, safety, and environmental considerations. Key chapters (3–6) include a discussion of best practices for controlling corrosion through chemical means. These chapters also provide examples of the successful application of the principles, including:

Understand the problem.

- Evaluate solution options.
- Design and execute control procedures.
- Evaluate the results.

Each chapter and most subtopics include reviews of current literature as well as a summary of the consensus of understanding from cited literature.

Definition of the Oil and Gas Environment and Need for this Book

The scope of this document is limited to corrosion-control methods in the production (upstream production) oilfield and pipeline/facility (midstream production) environments. This includes completions and completion fluids, the near-well bore area, natural or induced fractures, the screens,

perforations, tubulars, subsurface devices, gathering lines, production surface facilities, and transmission pipelines. This discussion does not specifically include cleaning or inhibition in refineries, but many of the necessary techniques and technologies are similar to those described in this book and could be applied with appropriate modifications. See Frenier[2] for a review of cleaning industrial equipment, including the downstream oil and gas environment.

The recent boom in new oil and gas production from shale plays has created vast opportunities for energy independence for North America as well as for a stable world economy. However, there is a great need for controlling corrosive attack to new (and existing) infrastructures. Chemicals for reducing various types of corrosion as described in this book provide an important (but not the only) tool for maintaing a constant flow of products and delivering them safely to consumers.

Design of this Book

Chapter 1 Introduction describes the scope of the book and introduces the types of oilfield equipment that requires corrosion protection. It also provides the chemical and mechanical bases for technologies needed to understand chemical methods of corrosion control. A list of terms and definitions are included.

Chapter 2 Review of Corrosion Causing Conditions in Oil and Gas Activities provides a short review of the key chemical and mechanical principles that cause the many manifestations of corrosion in connected oil and gas systems. Integrity management (IM) principles are described and the importance of chemical corrosion control is noted.

Chapter 3 Test Methods for Evaluating Corrosion and Inhibitors reviews the extensive literature describing corrosion test methods. This is an area where significant improvements in technologies have occurred during the past 30 years.

Chapter 4 Classic Corrosion Inhibitors Used in O&G Activities describes the very wide range of CI chemicals and particular uses for each type. Most engineers and oilfield chemists think of "corrosion inhibition" as the chemicals that block a metal's surface from attack. This author defines these as "Classic CI."

Chapter 5 Chemical Systems for Neutralizing or Removing Corrodents describes a diverse class of chemicals that act to remove or neutralize a corrosion-causing agent from the fluid stream. Included are oxygen scavengers, sulfide scavengers, and biocides.

Chapter 6 Application Methods for Corrosion Control Chemicals describes a wide range of application methods. Corrosion-control chemicals are not useful unless they can be placed into the fluid *before* corrosive agents contact a metal.

Chapter 7 HSE Activities as Applied to Corrosion Control Chemicals reviews the wide range of activities that are in use to safely and ethically apply corrosion-control chemicals in the diverse areas of our world.

Each chapter includes a summary with lessons learned. Chapters 3–6 also include a section with references and short abstracts of case histories that illustrate the principles described in the corresponding chapter.

Acknowledgments

I acknowledge the help and advice of Charles Trompler of Impact! Chemical Technologies. He provided significant insight into field operations. I also acknowledge the Society of Petroleum Engineers, T.D. Williamson, Ltd, Metal Samples Company, and Schlumberger, Ltd as sources for some of the illustrations in this book.

Contents

1

Introduction

This chapter introduces the requirements and uses of chemicals for controlling corrosion in the various segments of the oil and gas (O&G) environment. This chapter also reviews critical chemical and engineering concepts to help with understanding corrosion and control chemistries. Alternate control processes that are frequently used with or without chemicals are also noted. References are also provided at the end of the chapter.

Corrosion inhibitors and other corrosion control chemicals have been the subject of a wide variety of books as well as thousands of technical papers. A list of books that this author has used for reference and are especially related to corrosion inhibitors include: Nathan[3], EFC[4], Palmer[5], Raman[6], and Sastri[7]. Several books about oilfield chemicals that include many specific corrosion inhibitors and other control chemicals have also been consulted. These include Fink[8,9], as well as Kelland[10, 11]. A CorrCompilation from NACE International covering Microbiologically Influenced Corrosion (MIC)[12] is a useful addition to the corrosion specialists' library and has many useful reprints.

From approximately 1965 to 2005, the European Federation of Corrosion sponsored a series of symposia that were held in Ferrara, Italy. They were called the European Symposiums on Corrosion Inhibitors (Symposium européen sur l'inhibition de la corrosion—SEIC). They were numbered as SEIC 1–10 and were held on an approximate five-year schedule. This author does not know of any other worldwide series of meetings devoted entirely to corrosion inhibitors. However, specific Symposia on Corrosion and Scale Inhibitors were held at most of the annual Corrosion meetings[13], and the Society of Petroleum Engineers (SPE—Richardson TX) has had many seminars where corrosion and scale-control methods were discussed and documented. See the OnePetro website[14].

Many of the articles from SEIC will be cited in this book. Each meeting produced a volume of proceedings, and while these volumes are not easily found on the market today, some of the original papers were post-published for NACE International meetings and publications and especially in *Corrosion Science*[15].

1.1 Scope of Book

This book describes the use of corrosion-control chemicals ("inhibitors" and "scavengers") in all phases of the O&G well/transportation lifecycle.

The lifecycle of a well and the pipelines that connect wells to final customers greatly affects the need for chemical corrosion intervention. The lifecycle phases of a hydrocarbon-producing reservoir have been identified in the industry[16] as exploration (discover), appraisal (define), development (develop), production (deplete), and abandonment (dispose). See Figure 1.1 for explanations of chemistries used in the phases of a well system's activities.

Except for the earliest phases of exploration, where geologic and seismic methods find promising areas where hydrocarbons may be located, large volumes of chemicals are used to aid production. The chemicals are applied during the drilling, completion, production, and abandonment phases. However, *chemistry* is important in all phases, even when additional chemicals are not used. Find examples in subsequent text.

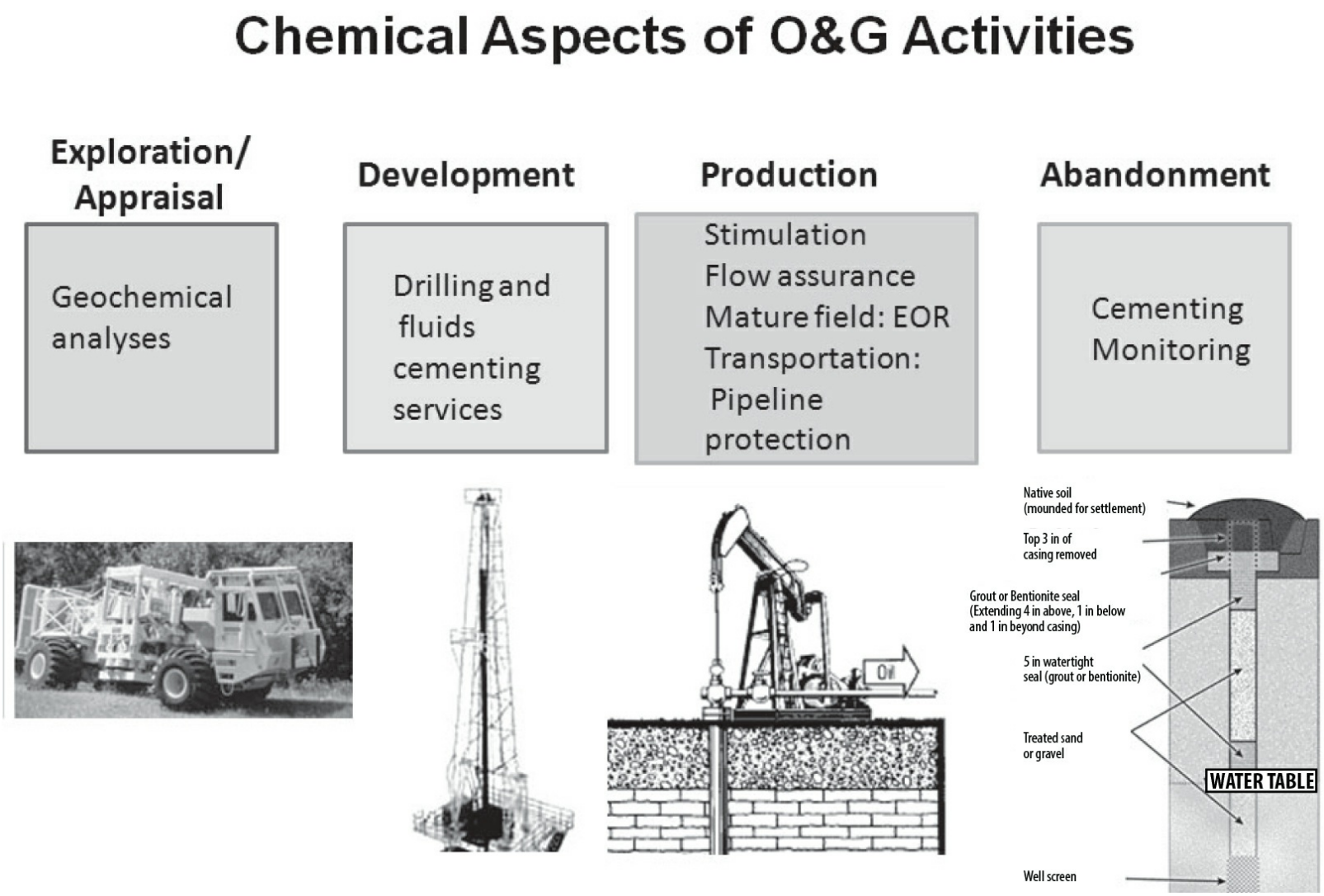

Figure 1.1 Chemistry in the Phases of a Well's Life

1. Exploration/appraisal: The geochemistry of the formation and chemistry of the fluids are determined.
2. Development: Drilling and cementing chemicals are applied to form and complete the well. Corrosion-control chemicals may be required in this phase.
3. Production: Chemicals (including corrosion-control materials) are applied in:
   - Stimulation treatments (acidizing [inhibitors needed] and fracturing)
   - Flow assurance (FA-controlling corrosion, scale, and other problems)
   - Mature fields (Enhanced oil recovery–EOR activities are used, and frequently more water is produced and corrosion aspects may change)
   - Pipeline activities (Moving well fluids and finished products requires a wide variety of corrosion-control chemicals)
4. Abandonment: Cementing chemicals are applied to seal the well and monitoring is performed.

In *Exploration and Appraisal*, geochemical analyses are performed based on seismic and well-probe data and analyses of outcrops or cores. A report[17] by McCarthy has described the tests that geochemists have used to determine the hydrocarbon-producing potential of a formation from the collected rock samples. These include Total Organic Carbon (TOC) analysis to find the maximum amount of carbon in the rock, as well as a pyrolosis process, where the rock is heated to increasing temperatures and effluents are analyzed by several methods (described in the papers). Fluids may be

captured in test wells for evaluation; chemical probes may also be placed using wireline or coiled tubing. Short summaries of methods used to analyze the liquid samples are described in Chapter 3 of Frenier[18].

Various water-based and oil-based fluids are used in the drilling (*Development*) of most wells. Complex oilfield cements are then used to stabilize the production tubing and to isolate various zones from communication with the surface and from non-producing formations. Completion fluids may also be used to maintain and control the well's pressure balance. Residual effects of drilling and completion chemicals may necessitate the use of acids or HF to remove damage. See Frenier[19]. If acidic completion fluids are in use, corrosion inhibitors may be required. Chemicals to control H_2S and CO_2 corrosion also may be applied.

Various chemicals are applied during all *Production* and *Transportation* phases to control corrosion in well components, facilities, and in the various types of pipelines and piping. The use of corrosion-control chemicals to maintain product flow continues in the connected midstream transportation sector. The use of chemicals to control corrosion in the connected pipeline segments is a main focus of this book.

Many different types of chemicals may be used: The thermodynamic and kinetic parameters that characterize the reactions come into play as they are injected and react in the production and midstream flow paths. Treatments may be conducted using "mini-chemical plants" that are custom assembled on-site using a wide variety of portable equipment. Some injection equipment may be semi-permanent if needed by projected long-term plans.

Basic chemical and engineering principles that are required to understand the applications of production corrosion-control chemicals are also reviewed in this chapter. The dominant theme that is described in this chapter (and emphasized throughout the book) is that *similar* chemical and engineering practices are used in many and possibly all aspects of the oil and gas production/transportation environment. It is possible to understand many different procedures by understanding some basic principles. An additional dominant theme is that *surface active chemicals* are used throughout the processes in production tubing and in all of the connecting pipelines. These formulations react with the surfaces, with each other, and with the fluids in the lines. If these chemical/engineering processes are performed properly, improved corrosion control will be achieved. The application of many of these same principles for protecting pipelines are given in more detail in Frenier[20].

While corrosion control on the external as well as the internal surfaces of tubing and pipelines is critical for maintaining system integrity, the primary scope of this book involves the use of chemicals to protect *interior surfaces*. Methods such as coatings and cathodic protection (CP) that are generally used to protect *external surfaces*, will be noted and referenced. See Goldsmith[21] for references to pipeline coatings and Lazzari[22] for cathodic protection information, as well as NACE[23] for a general review of pipeline corrosion control.

1.2 Definitions in this Book

This author provides a list of definitions of O&G related terms, since different names are used for various devices and conditions in different parts of an overall O&G system as well in different locations in the world-wide oilfield environment. A variety of names for various hydrocarbon products are also in common use. The source for many of the definitions is the Schlumberger Glossary[24].

Anode. This is the area of an electrochemical cell where *oxidation* takes place.

Anaerobic. Free of air or uncombined oxygen. This term frequently applies to a type of microorganism as well as the conditions in a specific environment.

Anomalies. This word is very important to the use and interpretation of internal line-inspection (ILI data, see Frenier[20]) procedures. It refers to signals from tools that *could* indicate a crack, dent, or corrosion pit. These devices are so sensitive that hundreds of anomalies could be identified in a line and sorting out the importance of each one is a key part of the data-analysis process. A report[25] by the USDOT notes that technically speaking, an anomaly is a *possible* deviation from otherwise sound material in a pipe or weld. Indication of an anomaly may be determined by nondestructive examination, such as inline inspection.

Cathode. This is an area of an electrochemical cell where *reduction* takes place.

Cathodic Protection. This is an important corrosion-protection process usually applied to external metal surfaces. The applications of DC voltages are designed to *polarize* the metal as a cathode and thus impede corrosion.

Coatings (protective). A wide variety of protective coatings are deposited on the exterior as well as some interiors of O&G units. These can be organic (resins and polymers of many types) as well as inorganic (galvanized, nickel, chromium-plated). Different layers of inorganic and organic coatings also may be applied. See Goldschmidt[21] and Munger[26]. The difference between an inhibitor film and a coating is usually associated with thickness and permanence of the film or coating.

Computational Fluid Dynamics (CFD). CFD is concerned with the efficient numerical solution of the partial differential equations that describe fluid dynamics.

Condensate. A low-density mixture of hydrocarbon liquids that are present as gaseous components in the raw natural gas produced in many oil and natural gas fields. It condenses out of the raw gas if the temperature falls below the hydrocarbon dew-point temperature of raw gas. It may contain some C_1-C_{12} aliphatic hydrocarbons as well as branched, cyclic, and aromatic molecules. It is similar in composition to natural gas liquids (NGL), defined below.

Corrosion Inhibitor. A chemical agent that reduces the *rate* of various corrosion reactions by protecting the surfaces of a corrodible metal. This is a major subject in this book.

Crude Oil. This is a general term that describes unrefined petroleum products and specifically petroleum liquids. The chemical compositions of crude oil streams vary from formation to formation,