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Oilfield Chemistry and its Environmental Impact

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To my dearest wife, Hazel, without whose tolerance, patience, support and love, this book would not have been possible.

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Preface

In writing this book I have designed it primarily as a reference book for chemists and environmentalists practicing in the upstream oil and gas industry. The oilfield presents a large number of technical challenges to the chemist and many of these are set against a background of increasing regulation and control of environmental impacts. This book focuses on the key chemistries used across the oilfield as defined by various upstream oil and gas exploration, drilling, development, production, processing and transportation. It is an attempt to be as comprehensive as reasonable, however other sources should be consulted particular in reference to particular chemistries or issues of interest. The work includes chemistries used in cementing, completion, work-over and stimulation, and further covers a number of chemistries involved in enhanced oil recovery, however these areas are not as comprehensively covered as others such as drilling and production.

A number of other books and reference works have examined the subject matter but all from the viewpoint of function and then chemistry applied. This book is an attempt to look at chemistry types and their use and potential use alongside their actual and possible environmental impacts. In the final two chapters I have attempted to focus on issues concerned with the environmental impact and fate of chemicals used in the oilfield sector. An outline of the regulatory conditions in a number of regions of the globe is included as well as also a critique of these in terms of overall environmental protection and sustainability.

The organisation of the book is laid out to examine specific chemistry types (Chapters 2–8) with Chapter 1 laying out the historical context of the subject, from its early application as a fairly piecemeal approach to solving certain oilfield problems, to its development into a fully-fledged chemical discipline. Chapter 8 also includes the key area of formulation as this is a critical part of the application of chemicals to the oilfield as rarely can neat products be added or used directly. Chapters 9 and 10 are concerned with environmental issues which in the last 20 years have been a critical part of the discipline and a growing requirement for any oilfield chemist to understand. Chapter 10 is particularly focused on issues of sustainability which at the time of writing are becoming of growing importance and I believe will become vital in the continued use of chemicals and the application of chemistry to the oilfield.

I would like to acknowledge the works of Professors Johannes Fink and Malcolm Kelland whose books on 'Oilfield Chemicals and Fluids' and 'Production Chemicals' respectively were an invaluable source of information and guided me to numerous primary references. Laurent Schramm's seminal work on oilfield surfactants was of particular use in Chapter 3, and Malcolm Stevens third edition in Polymer Chemistry kept me on the straight and narrow in Chapter 2.

Both the Royal Society of Chemistry and Society of Petroleum Engineers library databases were extremely useful in affording primary sources of chemicals and chemistry applied in the oilfield context.

Finally, I would like to thank my daughter Dr Emma Craddock for her invaluable sense check on the critique and argument in Chapter 9.

Oilfield chemistry is a fascinating subject and continues to excite and stimulate and is sure to do so into the future. It is hoped this book will aid chemists and others to enjoy it further.

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Introduction and History

This book is designed as a reference book for chemists and environmentalist examining the chemistry used in the oilfield and the environmental issues it can present. It is an attempt to be as comprehensive as reasonable and focuses on the key chemistries used across the oilfield as defined by various upstream oil and gas exploration, drilling, development, production, processing and transportation. It includes chemistries used in cementing, completion, workover and stimulation and further covers a number of chemistries involved in enhanced oil recovery (EOR). A number of other books and reference works have examined the subject matter but all from the viewpoint of function and then chemistry applied. This book is an attempt to look at chemistry types and their use and potential use alongside their actual and possible environmental impacts. The final two chapters are particularly concerned with the environmental impact and fate of chemical additives and chemical derivatives used in the oilfield sector, this contains an outline of the regulatory conditions in a number of regions of the globe and also gives a critique of these in terms of overall environmental protection and sustainability.

Oil production, as we know it today, originated in the mid-nineteenth century; however it was not until the twentieth century that the application of chemical inhibitors, particularly in the application of drilling additives such as lubricants and additives to separate oil and water and in corrosion protection, came into being.

As early as 1929, the physical chemistry around oil production was being investigated [1], and the limitations of experimental design in trying to reproduce the conditions in an oil well were becoming apparent.

In the early 1930s, there was a fundamental shift to a more scientific approach to the design and development of drilling fluids [2]. Until then drilling muds were considered as coarse suspensions and were formulated based on empirical knowledge as to their properties. However, the amount of field experience gained and theoretical knowledge to that point set the stage for an efficient programme of laboratory study and also the well economics, which can be effected by improved mud techniques. In particular laboratory work was undertaken to understand the functions of mud fluids and the properties necessary for their effective operation, such as weight, plasticity, viscosity, suspension efficiency or settling rate, permeability, non-gas cutting, maturity, gelling and gel strength and hydrostatic efficiency stability. It was also found that certain difficulties frequently occurred when drilling in limestone reservoirs.

1.1 Demulsifiers

One of the earliest production and processing problems encountered by the oilfield pioneers was the separation of crude oil from production water. There is anecdotal evidence of soaps and other detergent-based materials being used in oil wells in the late nineteenth century in the United States. This has a certain logic as it was already known that such materials or more correctly the surfactants they contain do act upon oils and fats, allowing their separation in water particularly if they have formed emulsions. These early soap products were at best able to aid in resolution at high concentrations added; however, the resulting water quality is likely to have been poor alongside the crude needing further treatment and/or settling. Over the years, however, better products and processes have resulted in a range of polymer- and surfactant-based demulsifiers and also a reduction in the demulsifier concentration required. This has come about due to a greater understanding of how surfactants work (see Section 3.1) and improvements in demulsification technology, which have been concentrated in the following areas:

- Chemical synthesis of new demulsifiers
- Development of laboratory and field techniques for testing demulsifier combinations
- Improvements in the engineering design of surface treating facilities, e.g. more favourable conditions for chemical emulsion destabilisation, forced coalescence in pipelines and treating units, faster and more efficient settling and cleaner phase separation

In modern crude oil production, efficient separation, dehydration and desalting of the crude oil, as well as treatment of effluent water to an environmentally acceptable level, are critical. In order to achieve this in a time-efficient manner and to ensure continuous and smooth oil production operations, demulsifiers have become a critical part of oilfield operations. Chemical demulsifiers are specially tailored to act where they are needed – at the oil/water interface, and their high efficiency at low dosages makes their use a very attractive economic way to separate oil and water [3].

In the 1940s the industrial availability of ethylene oxide (EO) allowed the production of fatty acid, fatty alcohol and alkylphenol ethoxylate nonionic surfactants, and this resulted in the first use of nonionic surfactants as demulsifiers in crude oil production [4].

With the creation of ethylene oxide/propylene oxide (EO/PO) block copolymers, the first 'genuine' demulsifiers were available. Addition of EO and/or PO to linear or cyclic (acid- or base-catalysed) alkylphenolformaldehyde resins and to diamines or higher functional amines yields classes of modified polymers that perform quite well at relatively low concentrations. Furthermore, these demulsifier bases were converted to high molecular weight products by reaction of one or more with difunctional compounds such as diacids, diepoxides, di-isocyanates and aldehydes, delivering a host of potential emulsion breakers. Over the decades many other classes of demulsifier were developed alongside better understanding of testing in 'live' oil situations. In recent years demulsifier development has focussed on the development of products to be environmentally acceptable [5], achieve good separation at low temperatures [6] and be effective in heavy waxy or asphaltenic crudes [7].

Significantly chemical demulsifiers have not only aided to the economics of modern oilfield production processing but also, by ensuring clean phase separation to give 'clean' water, reduced potential hazardous discharges of highly contaminated produced water.

Alongside the development of demulsifiers, the behaviour and stability of oilfield emulsion had been studied extensively, and a number of factors were isolated as being responsible for their stabilisation, primarily by film-forming asphaltenes and resins containing organic acids and bases. The effect of pH was also established [8]. In crude oil–brine systems, an optimum pH

range over which the adsorbed film exhibits minimum contracted film properties. In this range, interfacial tension is high – frequently near its maximum value – indicating the absence of highly surface-active species; crude oil–brine emulsions generally show minimum stability and surfactant requirements for breaking these emulsions are significantly reduced – sometimes no surfactant is needed.

1.2 Corrosion Inhibitors

There is a long history of the application of chemical inhibitors for the protection of physical assets in the oilfield from the corrosive components of oil and gas production [9]. Chemical corrosion inhibitors used in the oilfield can be grouped into several common types or mechanistic classes: passivating, vapour phase, cathodic, anodic, film forming, neutralising and reactive. The common material of construction in oil and gas production is carbon or low-alloy steel, so the primary aim is inhibition of the corrosive effects of fluids and gases on steel.

Inorganic inhibitors, such as sodium arsenite (Na_2HAsO_3) and sodium ferrocyanide, were used up to the early twentieth century to inhibit carbon dioxide (CO_2) corrosion in oil wells, but the treatment frequency and effectiveness was relatively poor [8].

The development of many organic chemical formulations that frequently incorporated film-forming amines and their salts began in the early 1920s, as with demulsifiers investigating the use of detergents and soaps. Significantly in the mid-1940s, long-chain polar compounds (surfactants) were shown to have inhibitive properties [10]. This discovery dramatically altered the practice of inhibitor application on primary production oil wells and gas wells. It permitted operation of wells that, because of the corrosivity and volume of water produced along with the hydrocarbons, would not have been produced due to economic considerations [8]. Perhaps entire reservoirs would have been abandoned because of the high cost of corrosion. Inhibitors also allowed the injection and production of high volumes of corrosive water resulting from the secondary recovery concept of waterflooding. Tertiary recovery floods, such as CO_2, steam, polymer and in situ combustion floods, would usually be uneconomical without the application of corrosion inhibitors.

Over the years there have been many improvements in inhibitor technology, mainly in formulation and application methods [11–13]. Until the turn of the century, it seemed a very settled question that the primary chemistries involved, in particular with regard to filming surfactants, could be selected from the following, either individually or in formulated combinations. These include primary amines, quaternary salts of amines and imidazolines [12, 14]. These filming protection agents act either by filming on the metal surface or by interacting and creating a bond with a variety of scales, e.g. calcium carbonate deposited on these surfaces [15].

At the present time, the filming protection mechanism is the most widely used agent in oil and gas processing and transportation due to necessity of good performance within a highly dynamic environment [16]. The mixture of produced fluids can give rise to a highly aggressive corrosive medium, which is then in direct contact with carbon steel, and to further challenge this environment to place these mixtures under conditions of high flow, creating a number of shear stress conditions [17]. Until recently chemical corrosion inhibitors have been sought, which have the ability to film within fluid mixtures at the interface between the liquid and surface, i.e. surfactant-like materials [18] (see Chapter 3), and also are persistent under conditions of high flow, i.e. have a certain amount of persistence to removal within these conditions [19]. These materials are, in general, excellent corrosion inhibitors under a variety of field conditions [20]; however they have certain limitations to performance, such as conditions of high temperature [21], and can be hazardous to the environment [22], often

having certain properties relating to marine toxicity and biodegradation, which make them less acceptable for use in the highly regulated offshore environments. In attempting to produce more environmentally acceptable corrosion inhibitors, a dilemma was observed in that the very technical effects that are being designed, for example, persistent materials, are not usually readily biodegradable. Similarly, a number of the chemistries are nitrogen based and possess inherent toxic properties [23]. These chemistries and many similar types are extensively explored in Chapter 3, alongside attempts to provide efficacious but environmentally acceptable products.

1.3 Drilling Fluids and Additives

Drilling fluids or 'muds' are probably among the oldest applied 'chemical' in the oilfield. The documented use of mud-ladened water for rotary drilling dates from the early twentieth century [24], but undoubtedly such products were already in common usage in such a way as to make them helpful to the driller, the operator or the engineer in solving his/her own special drilling problems. Alongside the use of these early water-based drilling fluids, the engineering particularly the tools and apparatus of the oilfield developed.

The materials encountered in wells drilled were varied, comprising unconsolidated sands, gravels and clays, in which thin layers of sandstones, shell conglomerates and shales would also be present. In these early days offshore drilling as we now come to think of it was not known; however many wells were drilled in tidal waters. All of this made it necessary for the oil exploration and production industry to start to employ specialists such as particular engineers, geologists and eventually oilfield chemists.

Drilling fluids are designed to exhibit thixotropic properties. Thixotropy refers to the property possessed by many suspensions of setting to form a jelly when allowed to stand undisturbed; this jelly can be broken down merely by shaking whereby the suspension reverts to the fluid condition. The change from jelly to liquid and liquid to jelly can be brought about in an indefinite number of times.

Thixotropy in drilling muds, particularly those to which reagents have been added, is largely due to the charges carried by particles in suspension and partly due to the size and shape of the particles. It may be that thixotropy is an intermediate stage between perfect stabilisation and complete coagulation of a suspension.

Over the years these muds have been refined and tailored to specific conditions and applications, and by the mid-twentieth century, three types of mud were established [25] as follows:

1) Clay freshwater-based muds
2) Organic colloids (both fresh-and saltwater based)
3) Water-based and oil-based blends (emulsions)

From field evidence and laboratory data, it was becoming possible to have a greater understanding of the drilling fluid on well performance. Over the coming decades until the present time, water-based drilling fluids have been a mainstay of drilling practices and well completion operations. However, as techniques have developed, chemical additives have been utilised to improve the rheological profile of the drilling fluid, aid in fluid loss control and ameliorate formation damage.

In the late 1930s, oil-based muds were being developed for drilling application. An oil-based mud is a drilling fluid in which oil has been substituted for water as the principal liquid ingredient. The composition of these muds was documented in the early 1940s and attempted to give through analytical techniques an understanding of the mud's characteristics and physical

properties [26]. Over decades this work has also been developed to relate the design of the mud and its composition to its desired physical properties.

In an oil-based mud, the oil acts as the continuous phase and water as the dispersed phase in conjunction with emulsifiers, wetting agents and gelling agents, which are mainly surfactant and/or polymer based. The oil base can be diesel, kerosene, fuel oil, selected crude oil or mineral oil.

Emulsifiers are important to oil-based mud due to the likelihood of contamination. The water phase of oil-based mud can be freshwater or a solution of sodium or calcium chloride. The external phase is oil and does not allow the water to contact the formation.

Oil-based muds are more expensive but are worth the cost when drilling through

1) Troublesome shales that would otherwise swell and disperse in water-based mud
2) To drill deep, high-temperature holes that dehydrate water-based mud
3) To drill water-soluble zones
4) To drill producing zones, particularly deviated or horizontal completions

The disadvantages of using oil-based muds are as follows:

1) Inability to analyse oil shows in cuttings, because the oil-based mud has fluorescence confusing with the original oil formation
2) Contamination samples of cuttings, cores and sidewall cores for geochemical analysis of TOC (Total Organic Carbon) masks the determination of the real API gravity
3) Contaminate areas of freshwater aquifers causing environmental damage
4) Disposal of cuttings in an appropriate place to isolate possible environmental contamination

In recent years, the environmental concerns from the disposal of oil-based muds and contaminated drill cuttings have been prominent in a number of regions, particularly in offshore drilling and completion, and this is discussed in greater detail in Section 8.3.3.

However, the development of oil-based muds has allowed a great extension to the range of temperatures and pressures that drilling operations can undertake and also the complexity of such operations. Undoubtedly the shale gas developments of the last few decades would not have occurred without the development of horizontal drilling techniques, and in turn these would not have occurred without the greater use and understanding of oil-based muds [27].

1.4 Cementing

It was becoming common practice to cement line wells by the early twentieth century, and cement plugging for the exclusion of water was documented in 1919 [28]. The objective in this early work was twofold:

1) To prevent the oil sand from becoming flooded
2) To plug off bottom water, thereby preserving the individual well and reclaiming production

Over the next decade or so, the use of cement in oil wells increased dramatically, leading to a large degree of variation in the types and specification used, which was recognised as inadequate as it was primarily based on typical construction cement. A uniform specification for oil well cements was adopted in the late 1930s [29]. This led to the definition of specific test work and desirable properties and an attempt to standardise this specification across the entire industrial sector. To date this has largely applied with chemical additives to cements being

allowed within specific parameters to achieve desirable properties pertinent to specific applications. Many chemistries have been used in achieving useful additives, and a number of examples are given throughout the following chapters. An additive of particular importance was the use of organic fluid loss additives [30]. These were developed for neat and gel cement slurries for use in squeeze operations to provide controlled dehydration of the slurry and, thus, fewer job failures. These materials were compatible with bentonite materials and all Portland cements, and did not adversely affect the physical characteristics of the set cement. They are effective over a wide range of well conditions and provide improved control of cementing treatments.

Fluid loss additives are now considered an essential component of any well cement. The fluid loss behaviour of a cement slurry basically occurs in two stages: (i) a dynamic one corresponding to the placement and then (ii) a static one, the waiting on the cement setting.

In general, these additives are based on polymers and in particular cellulose-type polymers; see Section 2.2.2. These materials are considered environmentally acceptable; indeed, they are PLONOR (pose little or no risk) listed materials [31], which means they do not have to be subjected to testing protocols; see Section 9.1.3. However, cellulose-type materials have several limitations: their fluid loss control properties decrease at temperatures above 200 °F, their salt tolerance is limited and over-retardation problems can occur at low temperature. Furthermore, the slurry viscosity to fluid loss ratio is unfavourable compared with that of synthetic fluid loss additives. When these cellulose-type materials are combined with other additives to help improve their performance, the environmental advantages are compromised and the resulting substance can no longer be listed as PLONOR. Modified cellulose materials have been developed to overcome this [32].

Additives of this type and others are considered across the following chapters of this book.

1.5   Well Stimulation and Improving Recovery

In the 1920s, the mechanisms that drive oil recovery were better understood [33], and the use of certain processes such as waterflooding was considered but was not deemed commercially viable.

In the 1930s, acid treatments on wells in carbonate reservoirs were being performed [34], which led to the study of acid treatment. This involved an analysis of the formation to be treated, the selection of a suitable type and amounts of acid, the time of treatments with respect to date of well completion and an economic analysis. The conclusion of the study was that it is considered good practice to use a properly inhibited acid, which practically eliminates the reaction of acid with steel and yet does not appreciably retard the action of the acid with limestone. These results and this objective form the basis of modern matrix stimulation practices.

Over the next 20 years or so, the understanding of what happens in acid stimulation developed and is discussed more fully in Section 5.6.2. Of particular importance has been the recognition of iron and iron salts being released during the stimulation process under certain conditions and need for its control [35]. Iron sulphide salts and free sulphur can be released, causing severe production impairment. Early treatments consisted of (i) making the plugging material water-wet with a non-ionic detergent, (ii) acidising to remove the iron salts, (iii) making the remaining free sulphur oil-wet with a surfactant, (iv) dissolving the free sulphur with a suitable solvent and (v) flushing all fluids into the formation. Standard practice is now to include a suitable sequestering agent to prevent the deposition of iron compounds following any acid treatment [36].

However, it is important to understand the acid treatment and design the chemical additive package appropriately. Many chemical additives for acid, including iron-control agents can be misused and overused with damaging results. Some agents precipitate if the expected downhole sources of iron are not present. In some cases, the iron actually keeps the sequestering agent in solution in spent acid. Thus, the effective use of iron sequestering agents depends upon the chemical conditions existing downhole during acid reaction. Since it is obviously impossible to know exactly what conditions will be encountered during an acid treatment, it is doubly important that care be used in selecting acid additives based on the best information available. The use of additives in acid stimulation is primarily discussed in Chapter 6.

1.5.1 Waterflooding

In the early 1930s, the use of waterflooding as a method of secondary recovery was being established indeed until that time there was only one place in the world where this method of rejuvenation was used on a large scale, that is, in the Bradford and Allegany fields of northwestern Pennsylvania and southwestern New York [37]. Here waterflooding was responsible for the complete revival of the Bradford field, which had been producing for sixty-two years. Although recoveries from flooding operations had been small, compared with the recoveries obtained from natural production in other producing districts of the world, they were nevertheless profitable.

Now the use of waterflooding as a means of secondary recovery is widespread and common practice. Indeed, the largest field in the world, the Ghawar, discovered in 1948 in the Eastern Province of Saudi Arabia, has a natural water drive support; therefore peripheral water injection was initiated to provide full pressure maintenance in 1968. Initially, water injection was conducted by gravity water injection. This was replaced by power water injection to provide flexibility in controlling the waterflood front propagation. The field has over 1500 wells, including producers and injectors both conventional and horizontal.

This use of water in maintaining reservoir pressure and production support, as well as a game changer in the economics of oil production, has had a significant effect on the complexion of oilfield chemistry. A large number of chemical additives used in the production of oil are really involved in water treatment, and these chemicals are described throughout the following chapters of this book, as well as some of the significant types such as scale inhibitors and biocides; see Section 1.6 by function being briefly detailed in this introductory chapter.

1.5.2 Enhanced Oil Recovery (EOR)

The previously described use of waterflooding has led on to more complex methods of improving and enhancing oil recovery. It is generally accepted that there are three primary techniques for EOR:

1) Thermal recovery
2) Gas injection
3) Chemical injection

Using EOR, 30–60%, or more, of the reservoir's original oil can be extracted [38], compared with 20–40% using primary and secondary recovery techniques [39]. Obviously, the techniques surrounding chemical injection have had the greatest bearing on oilfield chemistry and in particular the use of polymers and surfactants in EOR. These chemistries and their environmental consequences are substantially covered in Chapters 2 and 3, respectively.

1.6 Water Treatments

As stated in the previous section, the use of water has had a great influence on the chemicals used in oilfield activities; however, as equally important there has been a greater understanding of the chemistry of the water involved and occurring in the oilfield. This can be various types of water:

- *Connate water* that is naturally occurring in the reservoir and has been trapped in the pores of a rock during formation of the rock. The chemistry of connate water can change in composition throughout the history of the rock. Connate water can be dense and saline compared with seawater.
- *Formation water* or interstitial water in contrast to connate water is simply water found in the pore spaces of a rock and might not have been present when the rock was formed.
- *Produced water* is a term used in the oil industry to describe water that is produced as a by-product along with the oil and gas. Oil and gas reservoirs often have water as well as hydrocarbons, sometimes in a zone that lies under the hydrocarbons and sometimes in the same zone with the oil and gas.
- *Injection water* is the water used in secondary recovery, and its sources are usually aquifer or other freshwater sources (e.g. river), seawater or produced water (this is water being reinjected from oil production operations).

A full understanding of the chemistry of these waters is essential for an understanding of the oilfield chemistry that may be utilised in oilfield operations. These waters can be used for the make-up of drilling fluids, used in workover or enhanced recovery operations and utilised in waterflooding. They will require treatment to improve their quality usually by addition of a biocide and often with additional oxygen removal to aid in corrosion prevention. The chemistries involved here are given in a number of chapters of this book and are varied as they employ a number of chemistries from phosphorous products (Chapter 4) to simple organic molecules (Chapter 6) and complex polymers (Chapter 2). The use of water as a make-up and carrier solvent in oilfield chemical formulation is described in Section 8.2.1.

Although the use of water and its production was commonplace in the oilfield, it was not until the 1960s that analytical chemistry was applied to oilfield waters to give a full picture of the potential interactions that could occur [40]. Until that time water was seen as both a useful instrument in secondary recovery and a nuisance requiring disposal.

At this time, the importance of analysis of water chemistry was becoming important in geophysics in the understanding of oil and gas in sedimentary rocks [41]. These analyses were utilised by a number of oilfield disciplines, and from the water chemistry the design of chemical treatments was developed and improved as the water chemistry could be replicated in the laboratory and placed under simulated reservoir and production conditions.

1.6.1 Scale Inhibitors

Scale deposition was recognised as a problem in oilfield operations in the late 1930s, and particularly in waterfloods scaling compounds frequently were deposited away from the wellbore in flow channels of waterflood wells [42]. Mineral deposition in formation flow channels and on tubing, casing and producing equipment has been and continues to be a major problem in the upstream oil and gas industry. Compounds such as calcium carbonate, calcium sulphate and barium sulphate carried in the produced water can crystallise or precipitate as a result of a pressure drop, a temperature change, or exceeding the solubility of the product. This scaling reduces and sometimes even stops oil production by plugging the formation, perforations or producing equipment.

Acid, salts and phosphates were suggested as possible remedial treating chemicals. However, it was not until much later that the practical application of chemical scale inhibitors was developed and utilised. In the first half of the twentieth century, the regular remediation was extraction of equipment from the well, and the deposits were removed mechanically with scrapers and other such devices. Hydrochloric acid was also used when the plugging material was basically carbonate in nature [43].

In the late nineteenth and early twentieth century, natural products such as tannins were being used in boiler water treatments partly to prevent scale formation interestingly because of their environmental acceptability such products have returned to application, mainly as a flocculant for water clean-up; see Section 6.1 [44]. Throughout the 1950s and 1960s, a variety of polymer- (Chapter 2) and phosphorous (Chapter 4)-based scale inhibitors were applied to a number of scaling issues often with mixed success, especially where deposition was occurring at the near wellbore region. A critical advance was the controlled placement of chemical in the near wellbore to allow controlled release of scale inhibitor [45]. This was achieved using the extremely slow solubility di-metallic polyphosphates injected into producing zones in conjunction with fracturing. As a result of this type of treatment, scale deposition in the formation in addition to the wellbore and producing equipment was observed to be absent for a prolonged period of time and in some cases for over a year.

Over the next three or four decades, the use of placement technologies in the design of scale inhibitor squeezes has been highly successful in preventing scale deposition and the corresponding productivity declines. Alongside this, the understanding of how the chemistry of the scale inhibitor interacts with the formation has improved further the design and application of this chemistry [44, 46].

Scale inhibitors function at concentrations significantly below the levels required to sequester or chelate the scaling cations. The molar ratio of precipitate held in solution to inhibitor is typically on the order of 10 000 : 1. It has been postulated that scale inhibitors prevent, slow or distort crystal growth by blocking growth sites. It is also believed that these inhibitors prevent the adhesion of scale to metal surfaces in some unknown manner. Regardless of the inhibition mechanism, scale inhibitors must be present during scale nucleation in order to function effectively.

Numerous chemicals are effective inhibitors, but only four classes of compounds have been widely applied in the oilfield: polyphosphates, phosphonates, phosphate esters and polyacrylates/polyacrylamides. These are substantially described in Chapters 2 and 4.

An equally significant breakthrough was in the understanding of barium sulphate scaling [47], its study in the oilfield and application of suitable treatments, particularly of chemical inhibitors. This is discussed in more detail in Section 5.3.

In the late 1960s, it was established that the usual methods of studying oilfield mineral scale deposition in the laboratory do not work for barium sulphate because only small non-adhering crystals are formed. On the other hand, barium sulphate scale found in downhole or surface equipment is strongly adhering and may contain very large crystals. The difference derives from the extremely low solubility of barium sulphate. The firm adherence of scale and the consistent development of oriented crystals of 100 μ and larger, suggest a relationship between scale adherence and crystal growth.

In modern oilfield chemistry, much is now understood about scale deposition, and inhibition mechanisms [44] under various circumstances, from to the injection of seawater, causing barium sulphate deposition to the formation of the so-called exotic scales such as lead sulphide. Throughout the following chapters of this book, the reader will be introduced to a wide variety of chemistries that are used to treat, control, dissolve and inhibit the deposition of such inorganic scales.

1.6.2 Biocides and Bacterial Control

The organic origin of hydrocarbons has long been an accepted fact with nearly all geologists, with the weight of evidence favouring an organic origin. Crude oils themselves do not take long to be generated from appropriate organic matter. Most petroleum geologists believe crude oils form mostly from plant material, such as diatoms (single-celled marine and freshwater photo-synthetic organisms) and beds of coal (huge fossilised masses of plant debris). It is somewhat obvious that given the right conditions bacteria will also be able to exist on such organic material. In introducing water or disturbing the amount of natural water present, it is possible for bacteria to become established and grow. However, it was not until the late 1930s that an evidential link relating bacteria in the oilfield to production problems was established, in this case the role of anaerobic bacteria in corrosion [48].

In 1950 the role that bacteria play in waterflood operations had been definitively established [49, 50], and numerous observations had been made that indicated that bacteria are very effective in plugging the sand faces in water-input wells. A number of treatments had been developed including batch treatment with sodium hypochlorite (see Section 5.1.1), which is very effective in cleaning out bacteria-infested lines and water-injection wells; but most often the effect was not sufficiently permanent, and follow-up treatments were necessary. Chemical compounds belonging to the broad classification of alkyl and aryl high molecular weight amine salts and certain condensed EO–amines were applied as potential bactericide/corrosion inhibitors [50]. These products have strong surface-active properties and therefore have additional cleaning properties in the injector wells and also increase the permeability of the sand to water.

As secondary recovery techniques employing water injection became more economic, more numerous injection problems became more apparent. One of the most important is the tendency of porous rock around the wellbore to become partially plugged. It has been shown that this plugging is the result of both the deposition of inorganic materials such as ferric hydroxide and ferrous and ferric sulphide and the formation of bacterial deposits. Bacterial plugging occurs not only on the face of the formation but also within the matrix of the rock [51].

Studies have shown that most injection systems contain microorganisms of some type. Of the various microorganisms commonly found in oilfield injection waters, almost all have been shown to produce some degree of formation damage. Bacteria-laden waters often are responsible for much of the reduction in injection rate observed in input wells.

Oxidising agents such as calcium and sodium hypochlorite have been used in treating injection wells damaged by bacteria. The beneficial effect of these materials has been attributed to the oxidation of living or dead bacterial cells or other easily oxidised organic matter produced as the result of bacterial action [52].

In modern oilfield practice, the role of bacterial control is well established, and the main biocides and their application proven and usually highly effective if well managed and maintained. This is the case for managing bacteria from added water [53]. In the reservoir things may be more complicated [54], where recent work would indicate that biocides may only cause cell injury and not completely 'kill', particularly if the dose rates are sublethal. In alternative strategies, the role of biostatic agents particularly in competitive 'feeding' so that bacteria are unable to produce harmful waste products has gained some traction [55–57]. These products are mainly based on nitrite and nitrate salts and are more fully considered in a number of sections in Chapter 5, primarily in Section 5.9.4, but also in Chapter 6, Section 6.7, where anthraquinone is described as a biostatic agent.

It would appear that the use of biocides and the chemical types available in the oilfield is settled particularly in light of increasing regulatory controls in many parts of the world; see Chapter 9. However, the understanding of the microbial population in the oilfield is far from

complete, and new technologies in analysing and observing this population have opened a new door for further study [58].

1.7 Crude Oil Treatments

In the history of oilfield chemistry, the direct treatment of crude oil by deliberately designing chemical additives to change its properties, primarily its flow characteristics, is a relatively recent development. By contrast among the earliest crudes produced in what is recognised as the modern era, from the mid-nineteenth century onwards, are heavy crude oils [59]. The nature of paraffinic crudes was realised and, for the era, quite accurately determined in the 1920s where paraffin wax was isolated and its properties analysed, including the important recognition of the crude oil itself to aid in the solubility of the paraffin component [60].

Throughout the decades, the characterisation of heavy crude oils and the understanding of viscosity in crude oils developed. However, the main aids to producing heavier crude oils were by introduction of heat into the production process to keep the paraffin wax material from depositing and/or the addition of diluents materials such as aromatic solvents [61, 62]. Nevertheless deposition would often be problematic and be displaced from the flow lines to other equipment.

It was also noted that these 'waxes' also contained gums, resins, asphaltic material, crude oil, sand silt and in some instances water in addition to the wax crystals. In addition, the wax found in paraffin may range from the lowest to the highest melting point waxes present in the oil. The paraffin accumulations in wells in the same field will differ in percentages of wax of given melting points, since the conditions governing precipitation vary with each individual well [61].

1.7.1 Wax Inhibitors and Pour Point Depressants

It was not until the 1960s that direct chemical interaction to prevent wax depositing was proposed and developed, and at that time was known as crystal poisons [63]. Until then the main methods of paraffin deposition control were by regular mechanical removal, hot oiling and the maintenance of heat within the production system. Although this strategy was acceptable to an extent with onshore production, the advent of extremely deep production, offshore drilling and ocean floor completions, the application of such remedial measures becomes prohibitive economically. As a result, use of chemical additives as paraffin deposition inhibitors became more prevalent [64]. Since no one additive had proved to be universally effective, the selection of an efficient additive for a specific application becomes important, and as a consequence a better understanding of the mechanism of inhibition is also necessary. This has developed alongside the application of chemical additives.

Although pour point depressing additives were known in application in lubricating oils from the 1950s [65] and in refinery applications in the 1960s [66], it was not until over two decades later that their use in the oilfield was being reported [67, 68]. The majority of the chemistries developed for these applications are polymer based and are discussed throughout Chapter 2.

The mechanism of wax deposition has been studied extensively [69, 70]. Waxes are solids made up of long-chain ($>C_{16}$) normal or branched alkanes. These are naturally present in crude oils and some condensates. It has been conclusively established that normal alkanes, i.e. *n*-paraffin waxes, are predominantly responsible for deposition problems in pipelines; however wax deposition from paraffinic crudes can be both, a topside and downhole problem, blocking the flow of hydrocarbons as they are cooled during extraction and production [71].

The waxes in crude oils are much harder to control than those in condensates as they are composed of longer-chain alkanes. When the paraffinic wax is composed of alkanes of C_{16}–C_{25}, soft malleable waxes are observed. At higher molecular weights, C_{26}–C_{50} and greater, hard crystalline waxes are seen. The melting point of the wax is directly related to its molecular size and complexity; generally the higher the molecular size, the higher the melting point and the more difficult it is to keep the paraffin wax from forming deposits [72].

In the reservoir at high temperatures and pressures, any paraffinic waxes within the crude oil will be in solution. As the crude oil is produced, the temperature (and pressure) drops and wax will begin to precipitate from the crude oil if present in sufficient quantities and not solubilised by other components of the crude. Usually such precipitation or crystallisation occurs as the wax forming needles or plates [69].

As the pressure decreases, there is usually a loss of the lighter hydrocarbons to the gas phase. This reduces the solubility of the waxes in the crude oil.

In examining wax deposition, the most important measurement is the wax appearance temperature (WAT) or cloud point temperature. This is the temperature at which the first wax crystals begin to precipitate from the crude oil. It is not the same as the pour point. Typically, wax deposits when the pipe wall or other system surface temperature is below the WAT and below the temperature of the oil. The pour point temperature is generally reached when over 2% of the wax has deposited, whereas the WAT is observed when 0.05% or less of the wax has formed [69].

Wax deposition is considered to occur by two primary mechanisms:

1) If the surface (e.g. pipe wall) is colder than the WAT, then wax can form and deposit at this surface. This can occur even if the bulk fluid is above the WAT. This is known as the 'molecular diffusion mechanism'.
2) Already precipitated wax close to the surface will move to a region of lower velocity at the surface and deposit. This is known as 'shear dispersion'.

Therefore, wax deposition can occur by the first mechanism above and below the WAT, whereas the second mechanism only operates below the WAT. There are a number of other mechanisms and approaches, all of which contribute to the overall deposition effect; however by far the most significant effect has been shown to be the molecular diffusion mechanism [73].

Wax deposition and the WAT are both affected by the amount and type of asphaltenes present in the crude oil. In general, a significant amount of wax deposition is reduced in crudes containing high asphaltenic content [74].

In addition to deposition effects, waxy crudes exhibit problems related to increased viscosity and even gelation of the oil due to high amounts of wax precipitation. Crudes with a high paraffinic wax content are usually more prone to this problem. On cooling the waxes crystallise as plate-like arrays, which form a lattice structure, trapping the remaining liquid oil. This results in increased oil viscosity, decreased oil flow and reduced pressure in the pipeline [75].

1.7.2 Asphaltene Inhibitors, Dispersants and Dissolvers

Although there was some understanding of the composition of asphaltenes from as early as the early twentieth century, it was related to their constituency in bitumen and related materials and not as an overall component of crude oils. In the 1950s reports on the composition of asphaltenes began to appear [76]. In particular the understanding of the relationship between resins and asphaltenes began [77]. In addition understanding of the molecular structures and their properties in relation to a mineral oil residue was also reported [78]. From the early 1960s onwards, there has been an exponential growth in the study of asphaltenes and other