Chemistry for Enhancing the Production of Oil and Gas

Chemistry for Enhancing the Production of Oil and Gas

Wayne W. Frenier
Frenier Chemistry Consultants

Murtaza Ziauddin
Schlumberger

Society of Petroleum Engineers

Printed in the United States of America.

ISBN 978-1-61399-317-0

14 15 16 17 18 19 20 / 9 8 7 6 5 4 3 2 1

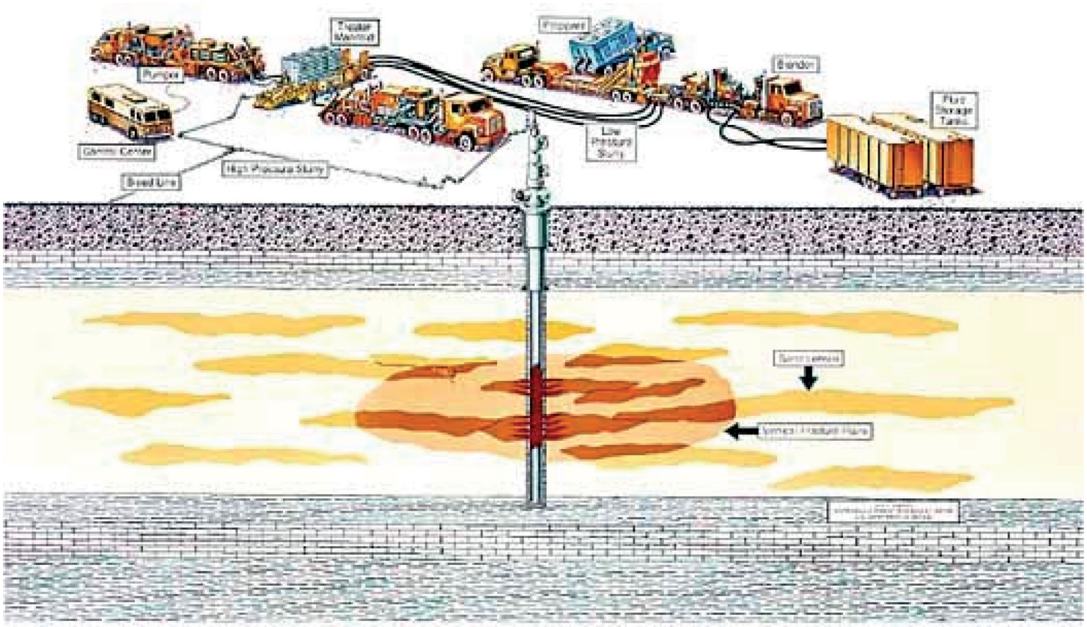
Society of Petroleum Engineers
222 Palisades Creek Drive
Richardson, TX 75080-2040 USA

http://www.spe.org/store
service@spe.org
1.972.952.9393

Preface

In approximately 1983, Al Look* (at that time the President of the Dowell Division of the Dow Chemical Company) noted that each day, hundreds (possibly thousands) of small chemical plants are set up in the world's oil/gas fields, and hundreds of thousands of pounds of chemicals are pumped into the Earth to enhance and maintain the flow of oil and gas. Frequently at the end of the treatment, these "mini-plants" [see **Fig. P.1** in API (2008) for drawing of a hydraulic fracturing set up] are broken down and transported to a new site. The chemistry applied is the same as might happen in a refinery or a chemical plant, but here, most of the reactions take place out of sight and control of the process engineers. Thus, the design of the *chemistry* is of particular importance because usually it cannot be changed once it is pumped. This book will describe how these underground reactions work to keep the world's hydrocarbon life lines flowing.

This document has been written to provide an improved understanding of the role of chemical reactions for enhancing and maintaining the production of oil and gas. There are several books that describe the thousands of production chemicals in use and include those by Fink (2003), Fink (2011), and Kelland (2009). These documents are useful references and have been cited frequently by the authors of this book. In addition, the reviews in Economides and Nolte (2000) have several excellent chapters (Constein et al. 2000; Hill and Schechter 2001) on some aspects of production chemistry and their applications in acid and hydraulic prop stimulation. This current book will also review many new aspects of the application of chemistry for enhancement oil and gas production that have reached the market since 2000 and will provide new mechanistic information.



---

*Al Look. 1983. Private communication.

This publication will provide an overview of the science and technology of the use of many production chemicals to a general technically trained audience, with emphasis placed on the basic chemical and physical principles by which the chemicals can enhance or maintain oil and gas production.

The introductory chapter describes the production environment, problems that require chemical intervention, and thus, the need for the thousands of different chemicals that are in use. This chapter also reviews the important chemical and physical principles that are common to most if not all of the enhancement treatments. This also places the technical aspects of production management in the perspective of the upstream oil and gas business. Subsequent chapters discuss aspects of the use and mechanisms of the complex chemistries that take place with the application of flow assurance chemicals, during stimulation (reactive chemistry and prop fracturing) and chemically improved oil recovery, including the use of chemical tracers. A separate chapter (Chapter 6) emphasizes the importance of health, safety, and environmental compliance in all aspects of oilfield treatments. Most of the chapters of the book end with a section where successful chemical enhancement or control methods have been used to solve specific production problems.

An outline for analysis is

- Is there a problem that requires an intervention?
- If there is a problem, how bad will it be?
- Can the problem be managed through engineering, and/or chemical means?
- Evaluate the results of an intervention or control strategy.

Each major section and most subsections will include reviews of current literature as well as summaries of the consensus understandings from the literature cited.

Chapter 1—Introduction

This section describes the reasons producing formations require intervention to enhance or maintain production, and the various types of chemical intervention in use. This chapter also reviews basic chemical and engineering processes that occur in production operations. It emphasizes the commonality of many of the chemical and engineering processes across the various production enhancement processes.

Chapter 2—Chemistry of Production Impairment

This chapter describes processes that impair the production of oil and gas such as formation damage and formation (and then mitigation) of emulsions in the production stream. It also updates techniques for mitigating and inhibiting deposition of inorganic and organic materials using references from earlier sources (Frenier and Ziauddin 2008; Frenier et al. 2010).

Chapter 3—Formation Stimulation With Reactive Chemicals

This chapter reviews the chemicals and mechanisms of reactive fluids (including acids) stimulation of oil and gas formations.

Chapter 4—Propped Fracturing Chemistry and Applications

This chapter discusses techniques and chemicals for formation stimulation using hydraulic fracturing using essentially nonreactive fluids.

Chapter 5—Improved Oil Recovery Chemical Applications

This chapter provides details of the chemicals and formation interactions that allow chemical sweep methods and conformance control processes to enhance hydrocarbon recovery. This chapter also gives a short review of the use of chemical tracers.

Chapter 6—Health, Ecology, and Safe Handling of Treating Chemicals and Produced Fluids

This chapter reviews general guidelines for planning and use of potentially toxic or hazardous chemicals that are frequently part of a treatment. Included is a discussion of the hazards associated with flowing back fluids. This chapter also reviews the use of chemicals to remediate spills of crude oil or production chemicals.

Chapters 1 through 5 each conclude with a "Things to Think About" section that summarizes the major findings revealed by the review of the technologies that were discussed and how this knowledge can be applied to chemical production management projects. Chapters 2 through 5 also have a section titled Histories and Best Practices (based on the technologies in that chapter). Here, the science and engineering principles described in the earlier sections are illustrated through practical demonstrations of chemical intervention and remediation.

Definition of the Upstream Oilfield Environment

The scope of this document is limited to chemical intervention and enhancement in the production ("upstream") oilfield environment. This includes the entire production field including injection wells, the producing formation, and especially the near wellbore area as well as flowlines and gathering lines. This includes the natural or artificial tubulars, subsurface devices, gathering lines, and wellsite surface equipment. The book *will not* describe chemicals in use to drill, complete, or cement the well field. See the books by Growcock (2005) and Nelson and Guillot (2005). The discussion will also *not* include problems in transmission pipelines or refineries. However, many of the techniques and technologies needed are very similar to those described in this book and could be applied with appropriate modifications. See Frenier (2001b) for a review of cleaning of industrial equipment, including the downstream oil and gas equipment.

Acknowledgment

The authors acknowledge the help and encouragement of Schlumberger Technology Company. In particular, we thank Schlumberger for releasing significant portions of text and illustrations from company files for use in the document. Olga Kresse, Bruno Lecerf, Philippe Enkababian, Eric Clum, and Greg Kubala, (all of Schlumberger) reviewed some of the portions of the text and provided very useful suggestions for improvements.We also acknowledge the help and encouragement of Prof. Mojdeh Delshad, University of Texas at Austin.

SPE would like to thank Mojdeh Delshad for his generous contributions to the oversight of this book project on behalf of the Books Development Committee. We appreciate his contributions in working with the author and ensuring that timelines and quality standards were upheld throughout the process.

This book is dedicated to my wife, Dolores, and our children, Andrew Frenier and Kathleen Turner, as well as our grandchildren. They inspire me to continue to work, learn, and become a better person.

–Wayne W. Frenier

I humbly dedicate this modest endeavor to the 52nd *Dai al Mutlaq*, His Holiness, Dr. Syedna Mohammed Burhanuddin (TUS), on the occasion of his 102nd birthday and 50 years as *Dai al Mutlaq*. I pray that Allah may grant him a long and healthy life.

–Murtaza Ziauddin

Contents

Chapter 1

Introduction

This chapter provides an introduction to the use of chemicals for production stimulation and maintenance of production after it has commenced. The life cycle of a well affects the need for chemical intervention. Many different types of chemicals may be used and the thermodynamic and kinetic parameters that characterize the reactions come into play as the chemicals are injected and react in the Earth or in the production flow paths. The treatments are conducted using “minichemical plants” that are custom assembled on site using a wide variety of portable equipment. For some applications, such as improved-oil-recovery (IOR) processes, the various chemical plants and storage vessels may be in place for several years.

Basic chemical and engineering principles that are required to understand the applications of production-enhancement chemicals also are 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 environment. So, 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 the producing formation and in the production tubing. These chemicals react with each other, with the fluids in the earth and frequently with the formation or with the solids in the tubing to *change* the flow paths of the hydrocarbons. If these chemical/engineering processes are preformed properly, improved production will be achieved.

1.1 Chemical Applications in the Reservoir Life Cycle

The phases of the life cycle of a hydrocarbon producing reservoir have been identified in the industry (POSC 2006) as exploration (discover), appraisal (define), development (develop), production (deplete), and abandonment (dispose). Except for the earliest phases of exploration where geologic and seismic methods are used to find promising areas where hydrocarbons may be located, large volumes of chemicals are employed. They are applied during the drilling, completion, production, and abandonment phases. However, *chemistry* is important in all of the phases (see **Fig. 1.1**) even when additional chemicals are not used. Examples are given.

- Exploration/appraisal: The geochemistry of the formation and chemistry of the fluids are elucidated.
- Development: Drilling and cementing chemicals are applied to help form and complete the well.
- Production: Chemicals are applied for:
    - Stimulation
    - Flow Assurance
    - Mature Field: IOR
    - Characterization: Tracers
- Abandonment: Cementing chemicals are used to seal the well and to monitor the seal.

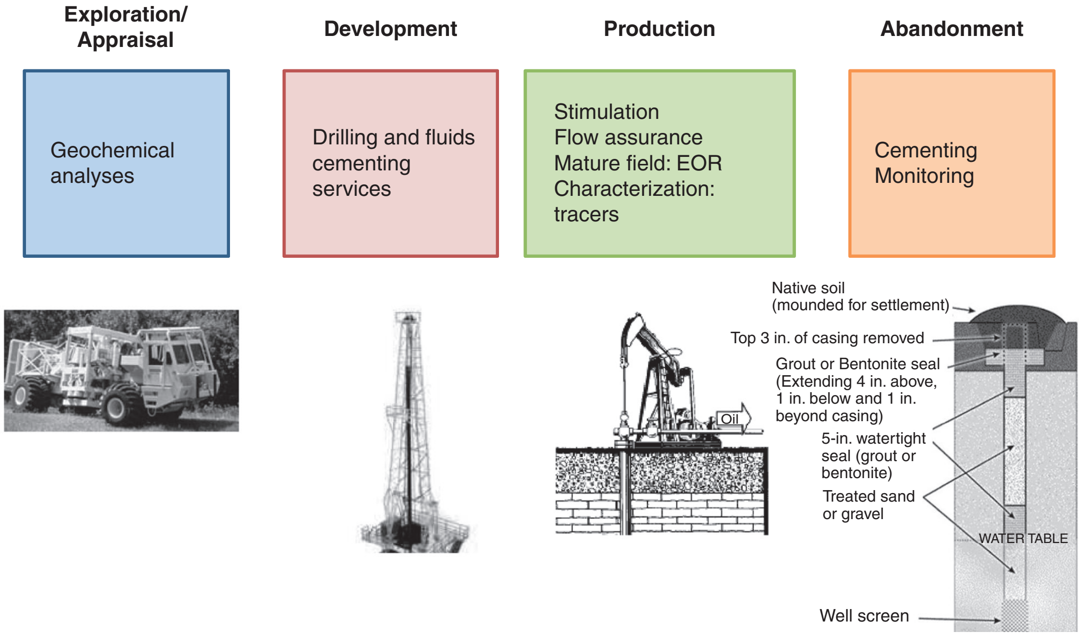


Fig. 1.1—Chemistry in the production phases of a well's life.

In "Exploration and Appraisal," geochemical analyses are performed based on seismic and well-probe data and analyses of outcrops or cores. McCarthy et al. (2011) has described the tests that geochemists have used to determine the hydrocarbon producing potential of a formation from the rock samples collected. These include total organic carbon 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 the effluents are analyzed by several methods described in the papers. Fluids may be captured in test wells for evaluation and chemical probes also may be placed using wireline or coiled tubing. Short summaries of methods used to analyze the liquid samples are described in Chapter 3 of Frenier et al. (2010).

Various water-based and oil-based fluids are used in drilling (development) most wells. Complex oilfield cements are then employed to stabilize the production tubing and to isolate various zones from communication with the surface and from nonproducing formations. Completion fluids also may be used to maintain and control the well's pressure balance.

Various chemicals are applied during all of the phases of Production to maintain, control, and frequently enhance the flow of the oil, gas, and aqueous phases. This is the major theme of this book. The production phase has sub phases based on the nature of production enhancements needed and are designated as Primary, Secondary, and Tertiary.

- *Primary:* In this phase, the reservoir fluids flow mostly because of the initial and internal pressure of the reservoir. Note that the production is controlled by the pressure differential between the formation and the bottomhole well pressure. While the pressures may be sufficient for initial production, stimulation using fracturing (Chapter 4) and/or reactive chemical treatments (Chapter 3) may be applied to some wells to remove formation damage or to improve returns from tight formations (such as shale plays). Other production chemicals can also be used to maintain flow (including inhibitors and surfactants described in Chapter 2 and in Frenier and Ziauddin (2008) and Frenier et al. (2010). For the most part, during the primary phase, chemicals (including any injected water or gas) are not added to the reservoir (except near the wellbore), so it is not changed significantly from a chemical standpoint. However, just by flowing the wells, important equilibrium conditions may be changed. At some point (either early or very late in the production phase) pressure maintenance may be required.
- *Secondary:* The pressure to move the fluids through the formations (see Section 1.2) can be maintained or enhanced by adding a downhole pump (to reduce the flowing pressure) or by

injecting fluids into the formation (Chapter 5). This presents a radical change to the reservoir since a large number of injection wells may be required. Many chemical treatments can be employed in this phase to maintain production including inhibitor injections as well as reactive chemical and prop fracture treatments. These are described in more details in Chapters 2, 3, and 4 of this book. At some point in the life of many reservoirs, the removal of additional hydrocarbons is not possible (or economically productive) because the oil is trapped in the pore spaces and so strongly adsorbed onto the rock surfaces that injection of water, natural gas, or steam cannot remove economic amounts. Because of uneven coverage of the reservoir because of permeability differences, oil also may have been bypassed by the sweep fluids. At this point, the massive injection of external chemicals may be planned, and the well may be considered to be in the tertiary production phase.

- *Tertiary:* As much as 2×10^{12} bbl of conventional oil and as much as 5×10^{12} bbl of heavy oil will remain in the world's reservoirs after the primary and secondary production has reached their economic limit (note that steam injection may be used at earlier phases in some heavy oil fields) (Thomas 2008). This incremental production is difficult and expensive but will remain as one of the methods for prolonging production from mature fields. Thus, the injection of large amounts of chemicals to remove some of this oil usually defines the tertiary phase. Much of the current interest is driven by the high price of oil.

Lastly, when the well is abandoned, cements and other chemicals are employed to make sure that the hydrocarbons or other fluids will not reach the surface or pollute aquifers or damage property.

The hydrocarbon chemical makeup, reservoir saturation, and morphology control the recovery of these valuable chemicals. The petroleum industry classifies "crude oil" using a number of different systems. These include classification by the location of its origin (e.g., "West Texas Intermediate, WTI (aka Texas Light Sweet)" or "Brent") and often by its relative weight (API gravity—defined below) and viscosity. Note that these are also pricing bench mark crude oils based on other characteristics but are typical from the region of origin. See the definitions in Wikipedia (2009a).

Refiners may also refer to the fluid as "sweet," which means it contains relatively little sulfur, or as "sour," which means it contains substantial amounts of hydrogen sulfide or mercaptans and requires more refining to meet product specifications. Low sulfur crude oil contains less than 0.5% sulfur and high sulfur oil may contain more than 2% sulfur (Simanzhenkov and Idem 2003). Each crude oil has unique molecular characteristics that can be determined by various analyses in petroleum laboratories and that are described in detail in Chapter 3 of Frenier et al. (2010). The petroleum production industry developed in stages and different terms have been, and continue to be, used to describe and characterize petroleum crude oil.

The API gravity of petroleum liquids is frequently used as a descriptor and is defined as

$$\text{API gravity} = (141.4/\text{Sp. Gr (SG) at } 60^{\circ}\text{F}) - 135.5. \qquad (1.1)$$

The temperature (60°F) and pressure (1 atm) will be specified for specific gravity. Usually, oils with higher API gravity values have a greater commercial value and lower API gravity value crude oils have lower commercial value. This general rule only holds up to 45°API gravity since beyond this value, the fraction of useable motor fuel that can be distilled from the liquid diminishes or is too volatile. Crude is also classified as light, medium, or heavy, according to its measured API gravity. Light crude oil is defined as having API gravity higher than about 30°API. Medium oil is defined as having API gravity between 20°API and 30°API. Heavy oil is defined as having API gravity below 20°API. Extra heavy oils are defined as API gravity below 10°API. In 1982, UNITAR (Kayhan 1982), an international working group, defined heavy oil to be gas-free oil between 100 cp and 10,000 cp at original reservoir temperature, with a density between 10° and 20°API gravity.

At a given pressure, the flow rate of a fluid is inversely proportional to the viscosity, so viscosity of the crude oil is an important value. The viscosity of the live oil is typically correlated with the gas content, API gravity, and temperature. Oil with high API gravity usually has low viscosity values. Oil that will not flow at normal temperatures or without dilution is usually called "bitumen" may have viscosities of >10,000 cp and the API gravity is generally less than 10°API. Bitumen derived from the oil sands deposits in the Alberta, Canada area has an API gravity of around 8°API. It is upgraded to an API gravity of 31°API to 33°API and the upgraded oil is known as synthetic oil. Theses upgraded fluids will have viscosity values less than 100 cp. See Beal (1946a, 1946b). The various chemical enhancement methods described in this book aid in the recovery of the hydrocarbon products and possibly at an increased rate.

A report (Freedoniagroup 2008) estimates the global oilfield chemical market at $15.2 billion and growing at 5.7%/year through 2012. There are thousands of individual chemicals employed in the various parts of the industry and many thousands of complex formulations that are custom-mixed each day to drill, complete, and treat the wells and auxiliary equipment associated with the upstream portion of the hydrocarbon supply chain. The books by Fink (2003), Fink (2011), and Kelland (2009) describe virtually all of the types of different chemicals employed in all of the phases of the life cycle of a producing reservoir and provide the identification of the structures of hundreds of these chemicals. These books cover different areas of oilfield chemicals (with some overlap) with thousands of references.

This current book concentrates on the chemical reactions and the application of chemical substances during the production phase to enhance and maintain the flow of oil and gas. Books by Growcock (2005) and Darley and Gray (1988) describe various aspects of drilling and completion fluid chemistries. Brooks (1992) and Nelson and Guillot (2005) review cementing chemistry and practice. There are many introductory books in chemistry that may be useful for further reading. The authors have consulted Solomons (1992a) in the Chapter 4 on frac fluids and Cotton et al. (1999) for references about inorganic compounds. The compilation by Clegg (2007) has been consulted for many engineering topics.

1.2 Need for Chemical or Engineering Practices to Enhance Production

Enhancing the performance of an oil and gas production system involves analyzing the system as a whole, identifying bottlenecks, and eliminating excessive energy dissipations or pressure losses in all system components. For optimal performance of the production system efficient use of energy is a must. The main components of the production system are

- The reservoir
- The completion, such as stimulation, perforation and gravel pack
- The tubing string
- The artificial lift system, such as pumps and gas lift valves
- The flow control devices, such as chokes and safety valves
- The surface flowline with chokes, valves, and elbows
- The separator and surface treaters

1.2.1 Analyzing Production Problems. Mach et al. (1982) introduced a systematic approach for analyzing performance of production systems. Their method involves defining computational nodes at various points in the system and calculating pressure as a function of flow rate for fluids flowing in and out of the node. **Fig. 1.2** shows a typical location of the computational node [large black dot (•) in the wellbore diagram]. Pressures at key points in the system are marked on the figure and are denoted as p_e, the pressure at the external reservoir boundary, p_{wf} for downhole flowing pressure, p_{wh} for pressure at the wellhead, and p_{sep} for pressure at the separator. For producing fluids from the reservoir to the surface, $p_e > p_{wf} > p_{wh} > p_{sep}$. Both inflow and outflow performance of the well must be considered.

Fig. 1.3a shows a plot of p_{wf} as function of flow rate for flow into the node, commonly known as the inflow performance relationship (IPR) curve. The equations in the figures are described later in the text.

The linear relationship between flow rate, q, and the downhole flowing pressure, p_{wf}, shown in the figure is for a single phase fluid flowing into the well from the porous reservoir rock. This relationship can be easily derived from the well known Darcy's law, which for horizontal, linear single phase flow of an incompressible fluid is expressed by Darcy (1857) and Dake (1995) as

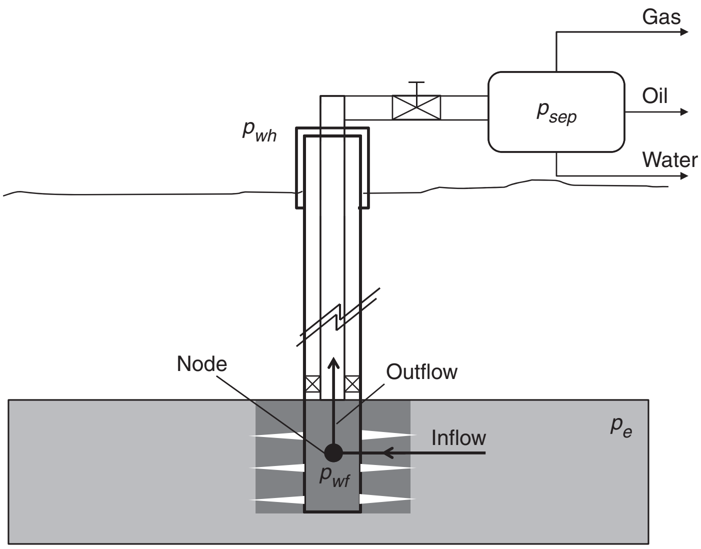


Fig. 1.2—An oil and gas production system showing the location of a computational node used in analyzing the performance of the system.

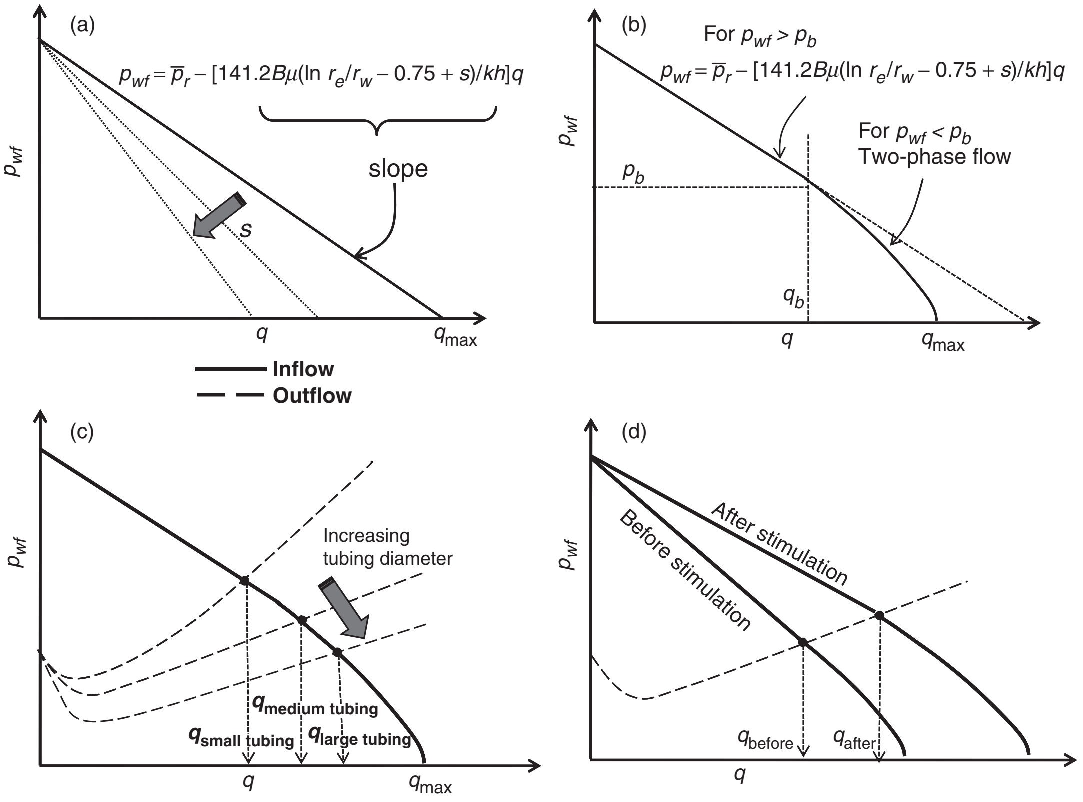


Fig. 1.3—(a) Inflow and outflow relationships for a node near the sandface, (b) inflow performance relationship (IPR) for flow of single-phase fluid, (c) inflow performance for two-phase fluid flow, and (d) outflow from the node for various tubing diameters.

$$q = \frac{Ak}{\mu}\frac{dp}{dl}, \qquad (1.2)$$

where q is the flow rate, A is the cross-sectional area, k is the permeability, μ is the fluid viscosity, p is the pressure, and l denotes distance, which is taken as positive in the *opposite* direction to the fluid flow. The permeability is the property of the porous medium and is a constant. Hence for a fluid with constant viscosity the flow rate is proportional to the pressure gradient (dp/dl). For flow of oil and gas into a vertical well, the radial form of Darcy's law is generally used. If flow from the reservoir into the well is taken as positive and the radial distance is taken as positive in the opposite direction, then the flow rate can be expressed as

$$q = \frac{Ak}{\mu}\frac{dp}{dr} = 2\pi rh\frac{k}{\mu}\frac{dp}{dr}, \qquad (1.3)$$

where, r denotes radial distance from the center of the wellbore and h is the height of the pay zone. Separating and integrating the previous equation and specifying the wellbore flowing pressure and the pressure at the external boundary, the expression for the flow rate in the well becomes

$$q = \frac{2\pi kh}{\mu}\frac{(p_e - p_{wf})}{\ln(r_e / r_w)}, \qquad (1.4)$$

where, p_e and r_e are the pressure and radial distance respectively to the external boundary, and p_{wf} and r_w, respectively, are the flowing wellbore pressure and wellbore radius. The previous equation can be rearranged and expressed as in terms of p_{wf} as

$$p_{wf} = p_e - q\left[\frac{\mu}{2\pi kh}\ln\frac{r_e}{r_w}\right]. \qquad (1.5)$$

Because the pressure at the external reservoir boundary is generally difficult to measure; a more useful form of the expression is in terms of *average* reservoir pressure, $\overline{p}_r$

$$p_{wf} = \overline{p}_r - q\left[\frac{\mu}{2\pi kh}\left(\ln\frac{r_e}{r_w} - \frac{3}{4}\right)\right]. \qquad (1.6)$$

This equation (Eq. 1.6) is for an undamaged well. Formation damage (**Fig. 1.4** and Section 2.3) may result in a region of reduced permeability near the wellbore, which may cause an additional pressure drop. A stimulation treatment, on the other hand, may reduce the pressure drop. The pressure drop, $p_{\Delta\text{skin}}$, because of a region of altered permeability near the wellbore was shown by van Everdingen and Hurst (1949) as

$$p_{\Delta\text{skin}} = \frac{q\mu}{2\pi kh}s, \qquad (1.7)$$

where s (frequently called skin) is dimensionless and accounts for the altered permeability near the wellbore.

Hawkin's formula is often used to estimate the skin effect, s (Hawkins 1956).

$$s = \left[\frac{k}{k_s} - 1\right]\ln\frac{r_s}{r_w}, \qquad (1.8)$$

where, r_s and k_s are the radial depth and permeability of the damaged or stimulated region. For an undamaged well $s = 0$, while for a damaged well, $s > 0$ and for a stimulated well $s < 0$. Adding $p_{\Delta\text{skin}}$ and converting to oilfield units the equation radial inflow of a single phase incompressible fluid into a vertical well becomes (see Fig. 1.3a)