CHARLES DIETZ
ID  UB2481SCH6186

PROGRESS IN OILFIELD CHEMICAL APPLICATIONS

THESIS

ATLANTIC INTERNATIONAL UNIVERSITY

CHARLES DIETZ
ID  UB2481SCH6186


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**Abstract:**

Achieving greater oilfield efficiency and productivity depends on wellsite operations that cost-effectively maximize recovery of oil and gas reserves, while minimizing the impact on the environment. Pivotal to these operations are specialty chemicals that impart unique capabilities and functionality for well drilling, completion and intervention services. The last decade's progress in upgrading chemical quality, deliverability and environmental compliance is paying off for operators in terms of field performance and longevity.

This thesis will describe types of chemical additives, solutions and compounds that are chemically formulated to achieve a specific purpose. That purpose being to optimize the performance and production of a hydrocarbon bearing reservoir. Secondly, but still of vital importance, is that any intervention done have minimal environmental impact.

**Chapter 1: General Introduction**

As crude oil resources decrease, the oil industry demands more sophisticated methods for the exploitation of natural resources. As a result, the use of oil field chemicals is becoming increasingly important.

The global market for oilfield chemicals will reach US$7.8 billion in 2006. (See chart M-1 in the appendix) Gains will be driven by more oil and gas exploration and production; a focus on difficult offshore and frontier areas; increasing well depths; and the need to maximize existing well output. The fastest growth will occur in new African, Asian and Latin American markets.

The old expression "garbage in, garbage out" has particular meaning when applied to oil and gas reservoirs. Hydrocarbon-bearing formations are highly susceptible to damage and plugging from a variety of sources—both natural and induced. The permeability and porosity of virgin reservoirs may be altered dramatically unless drilling, completion and intervention practices are conducted with the utmost diligence and attention to detail. If not, well productivity and ultimate reserve recovery suffer, while field maintenance, workover and environmental protection skyrocket. (1)

Many services performed in the oil field rely on specialty fluids and additives that fulfill specific functions within the wellbore or formation. This thesis will describe the types of specialty chemicals that are employed daily to drill and treat oil and gas wells and how a pervasive focus on their quality, reliability and deliverability is helping operators get the most from field developments. There will also be extensive discussion of the chemistry involved in the target process and effect of each of these families of chemical additives.

The Role of Specialty Oilfield Chemicals

Well drilling, completion, treating and workover fluids perform to their utmost because of the specialty chemicals that are added to impart unique properties and functionality. These chemicals fall into a broad variety of categories, with a staggering overall number of different compounds and blends. (See image M-1 in the appendix) If designed and manufactured to proper physical and performance standards—defined and confirmed through extensive field application—specialty chemicals become invaluable solutions to overcome problems that plague oil and gas wells throughout their lifetimes. (2)

If these chemicals are prepared, stored, mixed or pumped incorrectly, however, they can become a well's worst nightmare—leading to significant problems, such as plugging or precipitation, because of the presence of, and interactions caused by, inferior materials. Whether it's a drilling fluid that causes excessive formation damage or a fracturing fluid that leaves flow-restricting polymer residue in the proppant pace, increased costs, reduced efficiency and lower profits can be the end result of faulty selection or application. (3)

(1) Kruger RF: "An Overview of Formation Damage and Well Productivity in Oilfield Operations," *Journal of Petroleum Technology*. February 1986: 131-152.
(2) Drilling, Completion and Workover Fluids; Cementing; Fracturing; and Acidizing Supplements to *World Oil* (1996).
(3) Hawkins GW:"Laboratory Study of Proppant-Pack Permeability Reduction Caused by Fracturing Fluids Concentrated During Closure." paper SPE 18261, presented at the 63rd SPE Annual Technical Conference & Exhibiton, Houston, Texas, USA, October 2-5, 1988.

**Chapter 2: Definition of the Investigation**

During the boom years of the late 1970s and early 1980s, attention to chemical quality control and performance consistency was often lax. Operator and service company personnel and facilities were stretched to the limit just getting wells drilled and treated on schedule without costly mistakes. Often, there was simply insufficient time to fine-tune field formulations to achieve optimal results. The same was true for chemical suppliers, working all-out to satisfy demand for their products during a period of peak activity. There was little chance to concentrate on improving in-plant production and distribution procedures.

The situation was complicated further by growing demand for more sophisticated fluids. Over the years, simple fluids had given way to more complex ones. By the time the total depth of a well was reached, for example, a drilling mud might contain so or more distinct chemical types, many of which had been added to offset the effects of other components present during earlier phases of drilling. A large number of additives mean that a complicated set of chemical and physical interactions have to be thoroughly analyzed before the impact of the total fluid system on the formation can be understood.

Rising to the Challenge

Following the mid-1980s oil crisis, a new quality drive emerged throughout the oil field—reinforcing industry efficiency and productivity initiatives already in place. These initiatives first led operators and service companies to restructure and streamline their operations in an effort to improve profitability. Industry-wide consolidation and a refocusing on core competencies accompanied a host of cost-reduction steps.

When attention then turned to providing greater quality and value in each phase of the business, operators—concerned about the need to concurrently lower costs and improve well performance—began requesting more detailed information about the chemical additives present in fluids being pumped by service companies.

At the same time, a rising tide of public and governmental concern about health, safety and environmental issues—from personnel exposure to potentially harmful materials in chemical plants and at the rigsite, to protection of marine life and aquifer quality—prompted a concerted reevaluation of oilfield chemicals, and their effects on both the surface and subsurface. A host of regulations that had impacted oilfield operations since the 1970s and new legislation, enacted principally with the USA and the North Sea, combined to dramatically affect chemical approval, usage, handling and disposal. (See image M-2 in the appendix)

Governmental decrees, coupled with the industry's commitment to doing business in a more open manner, focused increased attention on fluids pumped into a well or discharged in the vicinity of the wellsite. Operators wanted details of any practices with potential negative impact so that they could fulfill obligations to regulatory agencies and answer questions from environmental groups. (4)

Specialty chemical suppliers were faced with a wide range of challenges and queries. To their credit, they reacted swiftly with a well-directed, comprehensive approach. As a result, there have been tremendous strides over the past decade in product quality control, reliability, deliverability environmental impact assessment compliance.

(4)  http://www.deh.gov.au/about/annual-report/04-05/legislation-epbc-appendix1.html

During the 1990s, the drive for continuous improvement and higher standards has led the oil field beyond regulatory compliance. The industry now expects more from itself and has begun to evaluate resource consumption and environmental burdens associated with oilfield activities. The concept of sustainable development—a belief that operators and service companies can meet the world's energy needs with compromising the environment for the future—is being employed at all levels to integrate quality and environmental goals into everyday business strategies and action plans. This evolution has been documented in over 360 papers published since 1992. (5)

Contemporary Oilfield Chemical Synthesis

Chemical manufacturing and blending plants are now operated to much stricter standards, with broader checks and balances on product quality. Advanced process control and optimization of reaction conditions have improved product reproducibility and increased product cost-effectiveness. In-plant safety and environmental awareness, packaging and inventorying, and distribution practices have been scrutinized and upgraded. At the same time, research conducted by service companies and specialty chemical manufacturers has led to a new crop of innovative, value-added materials and application methods that have extended the capabilities of well operations to deeper, higher temperature and higher pressure environments.

Given the number of raw materials, reaction intermediates and finished products—along with packaging, labeling and storage options—specialty chemical manufacturing plants are among the most logistically complex facilities to be found anywhere in the world. Today's plants have adopted quality and productivity programs that have been proven to be effective in other industries. Some have been introduced out of necessity, due to the complex nature of the operation. Others are a direct result of application of general quality standards, while still others reflect guidelines established through International Standard Organization (ISO) certification or mandated by environmental regulations. (6)

Compared to a decade ago, materials flow has been streamlined to simplify in-plant logistics and support new product delivery concepts, such as just-in-time manufacturing. For both liquid and dry products, the optimization process has affected the amount of space allocated to various functions—such as raw materials, receipt and storage, reaction and blending, packaging, finished product storage and shipment—as well as their proximity and interactions. The result: increased plant throughput, greater productivity of plant personnel, improved product delivery and shortened order lead times.

Several forces drive the reformulation—or reengineering—of specialty chemicals. The most notable are the need to improve performance, reduce cost and minimize safety or environmental hazards.

(5) SPE/UKOOA European Environmental Conference, Aberdeen, Scotland, April 15 – 16, 1997. The Third International Conference on Health, Safety and Environment, New Orleans, Louisiana, USA, June 9-12, 1996. The Second International Conference on Health, Safety, and Environment, Jakarta, Indonesia, January 25-27, 1994, "*Environmental Considerations*,"SPE reprint series,#37,1992.
(6) International Standards Organization, Geneva Switzerland. This family of programs has become the recognized standard for a quality system.

Chemical manufacturers and service companies have addressed these reformulation problems singly and in combination, with a beneficial impact on wellsite execution efficiency, well performance, environmental protection and overall chemical usage and cost.

Research studies targeted at improving the understanding of mechanisms controlling chemical interactions have led to revised material design specifications and extensions in functionality that allow field temperature and concentration ranges to be broadened. Process optimization within specialty chemical plants—centered on parametric studies of reaction and blending conditions such as temperature, pressure, exposure time and raw material addition sequencing—has increased product yield and reduced byproducts. Product consistency, reproducibility and reliability have improved, dovetailing directly with complementary programs geared toward quality control and quality assurance.

The oil crisis of the mid-1980s and enactment of environmental regulations have undoubtedly had the greatest impact on specialty chemical reformulation efforts. Chemical-cost reduction became a potentially quick and easy way to reduce wellsite costs and improve profitability in the face of depressed oil prices. As with replacement materials that broaden production and delivery capabilities, the main goal was to introduce alternative, lower-cost materials that do not demonstrate adverse effects, while still adhering to the product's original performance specifications.

For example, a high-volume corrosion inhibitor used in matrix acidizing stimulation treatments could no longer be produced because one of its key ingredients was no longer available. Thorough laboratory testing led to a suitable material that satisfied four objectives simultaneously, exceeding expectations established at the outset. The price of the final product could be reduced by 18% due to lower raw material costs and the new inhibitor demonstrated better dispersability in acid—a key criterion of product performance. Corrosion rates on samples of well tubing showed protection equal to the existing material, and the reformulated product posed reduced handling and mixing hazards.

Product reformulation, however, takes on its most important aspect when safety or environmental considerations come into play. The basic chemistry of many specialty oilfield products makes them potentially harmful if discharged into the environment. Reducing their impact may require elimination of materials banned by regulatory mandate or incorporation of components that offer reduced levels of toxicity. In both cases, the choice of replacements must be such that acceptable product performance is maintained. When environmentally sensitive materials form part of the reformulation equation, the evaluation and testing process becomes more complicated that in the case of replacing materials for cost or performance reasons. Interplay among composition, performance, toxicity and ultimate environmental impact must be considered, requiring a phased approach to design, testing, cross-checking and application. (7)

In 1995, a replacement program for specific products used in the North Sea was initiated at the Dowell product center in Tulsa. The initial objective was to replace eight chemicals, selection based on criteria established by clients and usage volumes. The goals were to eliminate any nonylphenol surfactants—which had been banned in selected areas of the North Sea—decrease product toxicity and improve biodegradability.

(7) O'Neill JE and Hill DG: "Reduction of Risk to the Marine Environment form Oilfield Chemicals—Balancing Environmental and Technical Needs," paper SPE 35946, 3rd International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, New Orleans, LA, USA, June 9-12, 1996.

Four products in particular—a stimulation surfactant, acid-corrosion inhibitor, acid-gelling agent and brine viscosifier—required extensive reformulation work.  Each presented the team of chemists working n the program with different challenges—dictated by chemical composition, complexity and intended use.  For the stimulation surfactant, a suitable reformulated product was developed that exhibited lower toxicity without a significant loss in product performance.  For the acid corrosion-inhibitor, an alternative product showed improved biodegradability for all but one component, and dramatically reduced toxicity.  Reformulation of the acid-gelling agent resulted in a product with equivalent performance, and eliminated the nonylphenol surfactant previously included.  Studies of brine viscosifier showed that novel chemistry would need to be developed before a long-term solution could be achieved. (8)

Minimizing Waste Discharge

Daily, millions of barrels of drilling and treating fluids are pumped into wells around the world.  The industry's goal is to pump the minimum volumes necessary to achieve design objectives—in other words, use the highest-performing, most time- and cost-effective fluids possible.  In most cases, this means minimizing the amount of fluid lost to the formation.  In wells that contact significant intervals of highly permeable formations, this in no small challenge.  Equally important—since the introduction of stricter environmental rulings—is the reduction or elimination of waste streams at the surface that require treatment or disposal, particularly since this treatment or disposal may be very extensive.

Information has now been presented that details the formulation, design theory, application, and environmental impact of chemical additives.  However, much of this has been generalized.  In the following section, more specific attention will be given to the applications of these additives and the chemistry responsible for their activity and effects.

(8)  http://www.glossary.oilfield.slb.com/Display.cfm?Term=viscosity

## Chapter 3: Dynamics of the Anticipated Solution

The textual discussion that follows is ordered according to applications and parallel job processes. In other words, information will first be presented that deals with drilling and associated chemical additives.  Next will be the production phase of hydrocarbon extraction.  Following in chapter four will be the transport of these products and chemical optimization utilized therein.  In chapter five, enhanced oil recovery theory and spill remediation will be presented.

Drilling Muds

Drilling fluids are mixtures of natural and synthetic chemical compounds used to cool and lubricate the drill bit, clean the hoe bottom, carry cuttings to the surface, control formation pressures, and improve the function of the drill string and tools in the hole. They are divided into two general types: water-based fluids and oil-based fluids.  They type of fluid base used depends on drilling and formation needs, as well as the requirements for disposition of the fluid after it is no longer needed.  Drilling muds are a special class of drilling fluids used to drill most deep wells. *Mud* (9) refers to the thick consistency of the formulation.

Following are the functions of a drilling mud:
1. To remove rock bit cuttings form the bottom of the hole and carry them to the surface.
2. To overcome the fluid pressure of the formation
3. To avoid damage of the producing formation
4. To cool and lubricate the drill string and bit
5. To prevent drill pipe corrosion fatigue
6. To allow the acquisition of information about the formation being drilled (e.g. electric logs, cutting analysis)

Muds can be classified on the basis of the following: fluid phase alkalinity, dispersion, and the type of chemicals used. (See Chart M-2 Appendix) (10)

Drilling fluids used in the upper hole sections are referred to as dispersed noninhibited systems.  They are formulated from freshwater and may contain bentonite. (A material composed of clay minerals, predominantly montmorillonite with minor amounts of other smectite group minerals, commonly used in drilling mud. Bentonite swells considerably when exposed to water, making it ideal for protecting formations from invasion by drilling fluids. Montmorillonite forms when basic rocks such as volcanic ash in marine basins are altered.) (11) The classification of bentonite-based muds is also shown in chart M-2 in the appendix.  The flow properties are controlled by a flocculant or thinner, and the fluid loss is controlled with bentonite and carboxymethylcellulose.

In nondispersed, noninhibited systems no special agents are added to deflocculate the solids in the fluid.  The main advantages of these systems are the higher viscosities and the higher yield point-to-plastics viscosity ratio.  These altered flow properties provide a better cleaning of the bore hole, allow a lower annular circulating rate, and minimize wash out of the bore hole.

(9)  http://www.glossary.oilfield.slb.com/Display.cfm?Term=mud
(10) W.C. Lyons. Standard handbook of petroleum and natural gas engineering, volume 1-2. Gulf Publishing Co, 1996.
(11) http://www.glossary.oilfield.slb.com/Display.cfm?Term=bentonite

Clear freshwater is the best drilling fluid in terms of penetration rate. Therefore it is desirable to achieve a maximal drilling rate using a minimal amount of solid additives. Originally low-solids mud formulations were used in hard formations, but they now also tend to find use in other formations. Several types of flocculants are used to promote the settling of drilled solids by flocculation.

Mud Compositions

Components for water-based muds are as follows: glycol, alkali silicates, acrylamide homopolymer, carboxymethylcellulose zinc oxide, acrylamide copolymer, and polypropylene glycol. Various modification methods for lignosulfonates have been described, for example, by condensation with formaldehyde(12) or modification with iron salts. (13) It has been found that chromium-modified lignosulfonates, as well as mixed metal lignosulfonates of chromium and iron, are highly effective as dispersants and therefore are useful in controlling the viscosity of drilling fluids and in reducing the yield point and gel strength of the drilling fluids. Because chromium is potentially toxic, its release into the natural environment and the use thereof is continuously being reviewed by various governmental agencies around the world. Therefore less toxic substitutes are desirable. The lignosulfonates are prepared by combining tin or cerium sulfate and an aqueous solution of calcium lignosulfonate, thereby producing a solution of tin or cerium sulfonate and a calcium sulfate precipitate. (14)

Oil-based muds are being replaced now by synthetic muds. Diesel oil is harmful to the environment, particularly the marine environment in offshore applications. The use of palm oil derivative could be considered as an alternative oil-based fluid that is harmless to the environment. (15) Hydrated castor oil can be used as a viscosity promoter instead of organophilic quaternized clays. (16) These muds can be visosified with maleated ethylene-propylene elastomers. (17) The elastomers are ethylene-propylene copolymers or ethylene-propylene-diene terpolymers. The maleated elastomers are far more effective oil mud viscosifiers than the organophilic clays used. On the other hand, specific organophilic clays can provide a drilling fluid composition less sensitive to high temperatures.

(12) S.V. Martyanova, A.A.Chezlov, A.G.Nigmatullina, L.A. Piskareva, and R.D. Shamsutdinov. Production of lignosulphonate reagent for drilling muds—by initial heating with sulphuric acid, condensation with formaldehyde, and neutralization of mixture with sodium hydroxide. Patent: RU 2098447-C, 1997.

(13) F.B.Ibragimov, A.I.Kolesov, E.A.Konovalov, N.T.Rud, B.M.Gavrilov, Ju.N.Mojsa, A.A.Rjabokon, and O.M.Shcherbaeva. Preparation of lignosulphonate reagent—for drilling solutions, involves additional introduction of water-soluble salt of iron, and anti-foaming agent. Patent RU 2106383-C, 1998.

(14) B.B. Patel. Tin/cerium compounds for lignosulfonate processing. Patent: EP 600343, 1994.

(15) A.A.M.Yassin and A.Kamis. Palm oil derivative as a based fluid in formulating oil based drilling mud. In *Proceedings Volume*, volume 2. 4th SPE et al Latin Amer Petrol Eng Conf (Rio De Janeiro, Brazil, 10/14-10/19), 1990.

(16) H. Muller, C.P.Herold, and S. von Tapavicza. Use of hydrated castor oil as a viscosity promoter in oil-based drilling muds. Patent:WO 9116391, 1991.

(17) C.K. Jones and D.B.Acker. Oil-based drilling muds with increased viscosity. Patent: EP 922743, 1999.

Synthetic-based muds are mineral oil muds in which the oil phase has been replaced with a synthetic fluid, such as ether, ester, PAO, or liner alkylbenzene, and are available from major mud companies.  The mud selection process is based on the mud's technical performance, environmental impact, and financial impact.  Synthetic muds are expensive.

Inverted emulsion muds are used in 10% to 20% of all drilling jobs.  Historically, first crude oils, then diesel oils and mineral oils, have been used in formulating invert drilling fluids. Considerable environmentally damaging effects may occur when the mud gets into the sea.  Drilling sludge and the heavy mud sink to the seabed and partly flow with the tides and sea currents to the coasts.  All of these hydrocarbons contain no oxygen and are not readily degraded. (18)

Because of problems of toxicity and persistence, which are associated with these oils, in particular for offshore use, alternative drilling oils have been developed.  Examples of such oils are fatty acid esters and branched chain synthetic hydrocarbons such as PAOs.  Fatty acid ester-based oils have excellent environmental properties, but drilling fluids made with these esters tend to have lower densities and are prone to hydrolytic instability.  PAO-based drilling fluids can be formulated to high densities and have good hydrolytic stability and low toxicity.  They are, however, somewhat less biodegradable than esters; they are expensive; and the fully weighted, high-density fluids tend to be overly viscous. (19)

During the drilling of oil and gas wells, a drill bit at the end of a rotating drill string, or at the end of a drill motor, is used to penetrate through geologic formations.  During this operation, drilling mud is circulated through the drill string, out of the bit, and back to the surface via the annular space between the drill pipe and the formation.  The drilling mud serves numerous functions including cooling and lubricating the drill string and drill bit, counterbalancing the pressures encountered in the formation using hydrostatic pressure, providing a washing action to remove the formation cuttings from the wellbore, and forming a friction-reducing wall cake between the drill string and the wellbore.  During drilling, the drill string may develop an unacceptable rotational torque or, in the worst case, become stuck.  When this happens, the drill string cannot be raised, lowered, or rotated.

Differential pressure sticking occurs when the drill pipe becomes imbedded in the mud wall cake opposite a permeable zone.  The difference between the hydrostatic pressure in the drill pipe and the formation pressure holds the pipe in place, resulting in a sticking pipe.  Differential sticking may be prevented, and a stuck drill bit may be freed, using an oil-mud or an oil- or water-based surfactant composition.

Such a composition reduces friction, permeates drilling mud wall cake, destroys binding wall cake, and reduces differential pressure.  Unfortunately, many of such compositions are toxic to marine life.  Synthetic PAOs are non-toxic and effective in marine environments when used as lubricants, return-of-permeability enhancers, or spotting fluid additives for water-based drilling muds.  A continuing need exists for other nontoxic additives for water-based drilling muds, which serve as lubricants, return-of-permeability enhancers, and spotting fluids.

(18) M.Hille, H.Wittkus, and F.Weinelt.  Use of acetal-containing mixtures. Patent US 5830830, 1998.
(19) K.F. Lin. Synthetic paraffinic hydrocarbon drilling fluid.  Patent US 5569642, 1996.

Olefin isomers containing between approximately 8 and 30 carbon atoms are suitable. However, isomers having fewer than 14 carbon atoms are more toxic, and isomers having more than 18 carbon atoms are more viscous. Therefore olefin isomers having between 14 and 18 carbon atoms are preferred. (20)

## Drilling Fluid Disposal

In response to effluent limitation guidelines promulgated by the EPA for discharge of drilling wastes offshore, alternatives to water- and oil-based muds have been developed. Thus synthetic-based muds are more efficient than water-based muds for drilling difficult and complex formation intervals and have lower toxicity and smaller environmental impacts than diesel or conventional mineral oil-based muds. Synthetic drilling fluids may present a significant pollution prevention opportunity because the fluids are recycled, and smaller volumes of metals are discharged with the cuttings than for water-based muds. A framework for a comparative risk assessment for the discharge of synthetic drilling fluids has been developed. The framework will help identify potential impacts and benefits associated with the use of drilling muds. (21)

## Drilling Fluid Loss

Fluid losses may occur when the fluid comes in contact with a porous formation. This is relevant for drilling and completion fluids, fracturing fluids, and cement slurries. The extent of fluid loss is dependent on the porosity and thus the permeability of the formation. Because the fluids used in petroleum technology are in some cases quite expensive, an extensive fluid loss may not be tolerable. Of course there are also environmental reasons to prevent fluid loss. The main mechanism of action to reduce fluid loss is porosity/permeability reduction by plugging the porous rock in some way. This can be accomplished via three main ways.
   (1) Macroscopic particles: suspended particles the clog the pores, forming a filter-cake with reduced permeability. (22)
   (2) Microscopic particles: Macromolecules that form a gel in the boundary layer of a porous formation. (23)
   (3) Chemical grouting: Resins that are injected in the formation that cure irreversibly.

(20) W.S.Halliday and D.Schwertner. Olefin isomers as lubricants, rate of penetration enhancers, and spotting fluid additives for water-based drilling fluids. Patent:US 5605879, 1997.
(21) A.F.Meinhold. Framework for a comparative environmental assessment of drilling fluids. Brookhaven Nat Lab Rep BNL-66108, Brookhaven Nat Lab, Nov. 1998.
(22) W.C.Chin. *Formation invasion: With application to measurement-while-drilling, time-lapse analysis, and formation damage.* Gulf Publishing Co., Houston, 1995.
(23) J.W.Dobson, Jr., J.C.Harrison, III, and P.D.Kayga. Methods of reducing fluid loss and polymer concentration of well drilling and servicing fluids. Patent: 697889,1998

Clay Stabilization

The problems caused by shales in petroleum activities are not new.  At the beginning of the 1950s, many soil mechanics experts were interested in the swelling of clays.  It is important to maintain wellbore stability during drilling, especially in water-sensitive shale and clay formations.  The rocks within these types of formations absorb the fluid used in drilling; this absorption causes the rock to swell and may lead to a wellbore collapse.  The swelling of clays and the problems that may arise from these phenomena have been the subject of numerous studies. (24) (25)

Clay minerals are generally crystalline in nature.  The structure of the clay crystals determines its properties.  Typically, clays have a flaky, mica-type structure.  Clay flakes are made up of a number of crystal platelets stacked face-to-face.  Each platelet is called a unit layer, and the surfaces of the unit layer are called basal surfaces.  A unit layer is composed of multiple sheets.  One sheet is called the octahedral sheet; it is composed of either aluminum or magnesium atoms octahedrally coordinated with the oxygen atoms of hydroxyl groups.  Another sheet is called the tetrahedral sheet.  The tetrahedral sheet consists of silicon atoms tetrahedrally coordinated with oxygen atoms.  Sheets within a unit layer link together by sharing oxygen atoms.  When this liking occurs between one octahedral and one tetrahedral sheet, one basal surface consists of exposed oxygen atoms while the other basal surface has exposed hydroxyl groups.  It is also quite common for two tetrahedral sheets to bond with one octahedral sheet by sharing oxygen atoms.  The resulting structure, known as the Hoffman structure, has an octahedral sheet that is sandwiched between the two tetrahedral sheets.  As a result, both basal surfaces in a Hoffman structure are composed of exposed oxygen atoms.

The unit layers stack together face-to-face and are held in place by weak attractive forces.  The distance between corresponding planes is adjacent unit layers is called the c-spacing.  A clay crystal sturcture with a unit layer consisting of three sheets typically has a c-spacing of about $9.5 \times 10_{-7}$ mm.

In clay mineral crystals, atoms having different valences commonly will be positioned within the sheets of the structure to create a negative potential at the crystal surface.  In that case, a cation is adsorbed on the surface.  These adsorbed cations are called exchangeable cations because they may chemically trade places with other cations when the clay crystal is suspended in water.  In addition, ions may also be adsorbed on the clay crystal edges and exchange with other ions in the water.

The type of substitutions occurring within the clay crystal structure and the exchangeable cations adsorbed on the crystal surface greatly affect clay swelling, a property of primary importance in the drilling fluid industry.  Clay swelling is a phenomenon in which water molecules surround a clay crystal structure and position themselves to increase the structure's c-spacing thus resulting in an increase of volume.

(24) C.Durand, A.Onaisi, A.Audibert, T.Forsans, and C.Ruffet. Influence of clays on borehole stability: A literature survey: Pt 2: Mechanical description and modelling of clays and shales drilling practices versus laboratory simulations. *Rev Inst Franc Petrol,* 50(3):353-369, May-June 1995.

(25) C.Durand, A.Onaisi, A.Audibert, T.Forsans, and C.Ruffet. Influence of clays on borehole stability: A literature survey: Pt 1: Occurrence of drilling problems physico-chemical description of clays and of their interaction with fluids. *Rev Inst Franc Petrol,* 50(2):187-218, March-April 1995.

Two types of swelling may occur. Surface hydration is one type of swelling in which water molecules are adsorbed on crystal surfaces. Hydrogen bonding holds a layer of water molecules to the oxygen atoms exposed on the crystal surfaces. Subsequent layers of water molecules align to form a quasi-crystalline structure between unit layers which results in an increased c-spacing. All types of clays swell in this manner.

Osmotic swelling is a second type of swelling. Where the concentration of cations between unit layers in a clay mineral is higher than the cation concentration in the surrounding water, water is osmotically drawn between the unit layers and the c-spacing is increased. Osmotic swelling results in larger overall volume increases than surface hydration. However, only certain clays, like sodium montmorillonite, swell in this manner.

Exchangeable cations found in clay minerals are reported to have a significant impact on the amount of swelling that takes place. The exchangeable cations compete with water molecules for the available reactive sites in the clay structure. Generally cations with high valences are more strongly adsorbed than ones with low valences. Thus, clays with low valence exchangeable cations will swell more than clays whose exchangeable cations have high valences.

Clay swelling during the drilling of a subterranean well can have a tremendous adverse impact on drilling operations. The overall increase in bulk volume accompanying clay swelling impedes removal of cuttings from beneath the drill bit, increases friction between the drill string and the sides of the borehole, and inhibits formation of the thin filter cake that seals formations. clay swelling can also create other drilling problems such as loss of circulation or stuck pipe that slow drilling and increase drilling costs. (26)

Mechanisms Causing Instability

Shale instability is an important problem faced during drilling. Stability problems are attributed most often to the swelling of shales. It has been shown that several mechanisms can be involved. These can be pore pressure diffusion, plasticity, anisotropy, capillary effects, osmosis, and physicochemical alterations. Three processes contributing to the instability of shales have to be considered: (27)

1. Movement of fluid between the wellbore and shale (limited to flow from the wellbore into the shale)
2. Changes in stress (and strain) that occur during shael-filtrate interaction
3. Softening and erosion caused by invasion of mud filtrate and consequent chemical changes in the shale

The major reason for these effects is of a chemical nature, namely the hydration of clays. Borehole instabilities were observed even with the most inhibitive fluids, that is oil-based mud. This demonstrates that the mechanical aspect is also important. In fact, the coupling of both chemical and mechanical mechanisms has to be considered.

(26) A.D.Patel, E.Stamatakis, and E.Davis. Shale hydration inhibition agent and method of use. Patent: US 6247543, 2001.
(27) L. Bailey, P.I.Reid, and J.D.Sherwood. Mechanisms and solutions for chemical inhibition of shale swelling and failure. In *Proceedings Volume*, pages 13-27. Recent Advances in Oilfield Chemistry, 5th Royal Soc Chem Int Symp (Ambleside, England, 4/13-4/15), 1994.

For this reason, it is still difficult to predict the behavior of rock at medium-to-great depth under certain loading conditions.

The stability of shales is governed by a complicated relationship between transport processes in shales (e.g., hydraulic flow, osmosis, diffusion of ions, pressure) and chemical changes (e.g., ion exchange, alteration of water content, swelling pressure).

Clays or shales have the ability to adsorb water, thus causing the instability of wells either because of the swelling of some mineral species or because the supporting pressure is suppressed by modification of the pore pressure. The response of a shale to a water-based fluid depends on its initial water activity and on the composition of the fluid. The behavior of shales can be classified into either deformation mechanisms or transport mechanisms. (28) Optimization of mud salinity, density, and filter-cake properties is important in achieving optimal shale stability and drilling efficiency with water-based mud.

Bacteria Control

Major problems in oil and gas operations result from the biogenic formation of hydrogen sulfide ($H_2S$) in the reservoir. The presence of $H_2S$ results in increased corrosion, iron sulfide formation, higher operating costs, and reduced revenue and constitutes a serious environmental and health hazard.

In secondary oil recovery, which involves waterflooding of the oil-containing formation, biofilms can plug the oil-bearing formation. Severe corrosion also can result from the production of acids associated with the growth of certain bacterial biofilms. These bacterial biofilms are often composed of sulfate-reducing bacteria, which grow anaerobically in water, often in the presence of oil and natural gases. Once biofilms are established, it is extremely difficult to regain biologic control of the system.

When biofilms are formed on metallic surfaces, they can seriously corrode performance production facilities, chemical processing plants, paper mills, ships, and water distribution networks. Microbiologically influenced corrosion(MIC) represents the most serious form of that degradation.

It is estimated that MIC may be responsible for 15% to 30% of failures caused by corrosion in all industries.

Thus an effective control of bacteria responsible for these undesired effects is mandatory. Several biocides and nonbiocidal techniques to control bacterial corrosion are available, and procedures and techniques to detect bacteria have been developed. A brief review of these procedures and techniques will follow.

Microbiologically influenced souring (MIS) is the production of $H_2S$ through the metabolic activities of microorganisms. A better chance for mitigating MIS in some down-hole environments using biocides may be possible if the problem is detected early in the souring process. (29)

(28) J.P.Tshibangu, J.P.Sarda, and A.Audibert-Hayet. A study of the mechanical and physicochemical interactions between the clay materials and the drilling fluids: application to the boom clay (Belgium) (etude des interactions mecaniques et physicochimiques entre les argiles et les fluides de forage: application a l'argile de boom (Belgique)). *Rev Inst Franc Petrol*, 51(4):497-526, July-August 1996.
(29) E.A.Morris,III,D.M.Dziewilski,D.H.Pope, and S.T.Paakkonen. Field and lab studies into the detection and treatment of (MIS) in natural gas storage facilities. In Proceedings Volume, 49th Annu NACE Int Corrosion Conf(94), Balt.MD,1994.

However, if the H2S-producing creatures are allowed to spread into subsurface regions that are less accessible to biocides (profuse-stage MIS), the problem becomes less mitigable by conventional means.

Treatment With Biocides

A special problem is the refracturing of a previously fractured formation that is contaminated with bacteria. In such a case the fracturing fluid must be mixed with an amount of biocide sufficient to reach and to kill the bacteria contained in the formation. The refracturing of the formation causes the bactericide to be distributed throughout the formation and to contact and kill bacteria contained therein. (30)
The intermittent addition technique(31-33) consists of :
1. The addition of a slug dose of a biologically effective amount of a quick-kill biocide.
2. Intermittent addition of biologically effective amounts of a control biocide. This means that the control biocide is dosed for a certain period of time, followed by a period of much lower or zero dosing. This cycle is repeated throughout the treatment.

This process reduces the amount of control biocide employed in the control of contamination of oil production system waters by sessile bacteria. The biocide may be applied at intervals of 2 to 15 days. The duration of biocide application is preferably from 4 to 8 hours. (34)

Nonbiocidal Control

Chemical treatments for bacteria control represent significant cost and environmental liability. Because the regulatory pressure on the use of toxic biocides is increasing, more environmentally acceptable control measures are being developed.

Biocompetitive Exclusion Technology

Besides adding biocides to wells, another approach seems to be promising—modifying the reservoir ecology. The production of sulfide can be decreased, and its concentration is reduced by the establishment and growth of an indigenous microbial population that replaces the population of sulfate-reducing bacteria.
The technology is based on the addition of low concentrations of a water-soluble nutrient solution that selectively stimulates the growth of an indigenous microbial population, thereby inhibiting the detrimental sulfate-reducing bacteria population that causes the generation of H2S.

(30) M.A. McCabe, J.M.Wilson, J.D.Weaver, and J.J.Venditto. Biocidal well treatment method. Patent: US5016714, 1991.
(31) B.M.Hegarty and R.Levy. Control of oilfield biofouling. Patent CA 2160305,1996.
(32) B.M.Hegarty and R.Levy. Control of oilfield biofouling. Patent EP706759, 1996.
(33) B.M.Hegarty and R.Levy. Procedure for combatting biological contamination in petroleum production (procede pour combattre l'encrassement biologique dans la petrole). Patent: FR 2725754, 1996.
(34) S.S.Moody and H.T.R.Montgomerie. Control of oilfield biofouling. Patent: EP 706974, 1996.

This deliberate and controlled modification of the microflora and reservoir ecology has been termed *biocompetitive exclusion.* (35) (36)

Biocides are often misapplied in the petroleum industry. Many of the misapplications occur because the characteristics of the biocides are not considered before use. Some guidelines(37) will be reviewed:

1. Early detection of microbiologic problems is imperative, and reparative actions must be taken as soon as possible.
2. These measures should include changes in operating methods to prevent degradation of the operating environment.
3. This would include the rejection of untreated waters for cleaning deposits in vessels and lines.

In general, biocides are needed to control the activity of the bacteria in a system. However, biocides alone will not solve a microbiologic problem. Five requirements for the bactericide selection are emphasized(38):

1. Wide bacteria-killing ability and range
2. Noncorrosive property, good inhibiting ability, and convenience for transportation and application
3. Nontoxic or low-toxicity property that causes no damage to human beings and is within environmental control regulations
4. Good miscibility, with no damage or interference to drilling fluid or its chemical agents
5. Bacteria killing effect that is not affected by environmental adaptation of the bacteria

Bacterial corrosion is often referred to as *microbiologically influenced corrosion*. MIC involves the initiation or acceleration of corrosion by microorganisms. The metabolic products of microorganisms appear to affect most engineering materials, but the more commonly used corrosion-resistant alloys, such as stainless steels, seem to be particularly susceptible. To adequately address MIC problems, interdisciplinary cooperation of specialists in microbiology, metallurgy, corrosion, and water chemistry is required. Because the complexities of MIC are so great, one single technique cannot provide all the answers in terms of corrosion mechanisms.

(35) D.O. Hitzman and D.M.Dennis. Sulfide removal and prevention in gas wells. In *Proceedings Volume*, pages 433-438. SPE Prod Oper Symp (Oklahoma City, OK, 3/9-3/11), 1997.

(36) K.A.Sandbeck and D.O.Hitzman. Biocompetitive exclusion technology: a field system to control reservoir souring and increase production. In *US DOE Rep* et al Microbial Enhanced Oil Recovery & Relat Biotechnol for Solving Environ Probl Int Conf (Dallas, TX, 9/11-9/14), 1995.

(37) J.Boivin. Oil industry biocides. *Mater Performance*, 34(2):65-68, Feb. 1994.

(38) Y.Zhou. Bactericide for drilling fluid. *Drilling Fluid Completion Fluid*, 7(3): 2A, 10-12, 1990.

Corrosion Inhibitors

The history of corrosion inhibitors and neutralizers and their invention, development, and application in the petroleum industry is documented by L.E. Fisher. (39)  Early corrosion inhibitor applications in each of the various segments of the industry, including oil wells, natural gas plants, refineries, and product pipelines, are reviewed.

Corrosion and scale deposition are the two most costly problems in oil industries. Corrodible surfaces are found throughout production, transport, and refining equipment. Corrosion inhibitors, which are used for the protection of oil pipelines, are often complex mixtures.  The majority used in oil production systems are nitrogenous and have been classified into the following broad groupings:

1. Amides and imidazolines
2. Salts of nitrogenous molecules with carboxylic acids (fatty acids, napthenic acids)
3. Nitrogen quaternaries
4. Polyoxylated amines, amides, and imidazolines
5. Nitrogen heterocyclics

Corrosion problems may occur in numerous systems within the petroleum industry.  These include: acid stimulation jobs, cooling systems, drilling muds, oil production units, oil storage tanks, oil well, protection of pipelines, refinery units, scale removal treatments using acids, steam generators, and technologic vessel.  Many compositions involve environmentally dangerous products, such as chromates, fatty amines of high molecular weights, imidazolines, etc.  The use of some of the alternatives, for instance, polyphosphate or polyphosphonate, is limited because they precipitate in the presence of the salts of alkaline earth metals or because of high costs.

Batch treatment of pipelines with liquid or gel slugs of inhibitor, with continuous injection as a backup (or vice versa), are accepted methods of corrosion prevention. (40) Batching liquid or gel inhibitors using pigs is more likely to attain complete coverage of the internal surface of the pipe wall than is continuous injection.  The film laid down is quite resilient and of long duration.  Important factors to optimize the application include determining film thickness and selecting an appropriate pigging system and program. Cleaning of the pipeline before inhibitor pigging is recommended.

The common method of treating rod-pumped wells is to periodically batch inhibitor into them.  The treatment period for a given well is selected using empirical rules based on well production volumes.  A successful and economic corrosion inhibition program must carefully control the inhibitor concentration in the well fluids. Environmental aspects and conservative inhibitor usage necessitate the measurement of very low corrosion inhibitor concentrations.  Inhibitor concentrations as low as one part per million are significant, thus requiring an analytic technique with a detection limit of a fraction of a part per million. Numerous spectrophotometric procedures are currently in use in the industry to provide the necessary quantitative results.

(39) L.E.Fisher. Corrosion Inhibitors and neutralizers: Past, present and future.
In Proceedings Volume. Annu NACE Corrosion Conf.(Corrosion 93)
New Orleans, LA, 3/7-3/12, 1993.
(40) M.A.Kennard and J.G. McNulty. Conventional pipeline-pigging technology:
Pt 2: Corrosion-inhibitor deposition using pigs. Pipes Pipelines Int, 37(4):
14-20, July-August 1992.

## Corrosion Inhibitors (41)

| | |
|---|---|
| Acetylinic alcohol (a) | Polyphosphonohydroxybenzene sulfonic acid compounds (f) |
| Tall oil fatty acid anhydrides | 1-Hydroxyethylidene-1, 1-disphosphonic acid (g) |
| 3-Phenol-2-propyn-a-ol(PPO) (b) | 2-Hydroxyphosphono-acetic acid (h) |
| Dicyclopentadiene dicarboxylic acid salts(c) | Water-soluble 1,2-dithiol-3-thiones (i) |
| Hydroxamic acid | Sulfonated alkylphenol (j) |
| Cyclohexylammonium benzoate | Polythioether |
| Acyl derivatives of tris-hydroxy-ethyl-perhydro-1,3,5-triazine | Thiazolidines |
| 2,4-Diamino-6-mercapto pyrimidine sulfate (DAMPS) combined with oxysalts of vanadium, niobium, tantalum or titanium, zirconium, hafnium | Substituted thiacrown ethers pendent on vinyl polymers |
| Aqueous alkanol amine solution (d) | Benzylsulfinylacetic acid or benzylsulfonylacetic acid |
| Quaternized fatty esters of alkoxylated alkyl-alkylene diamines | Halohydroxyalkylthio-substituted and dihydroxyalkylthio-substituted polycarboxylic acids (k) |
| Mercaptoalcohols | Alkyl-substituted thiourea |
| Polysulfide (e) | 2,5-bis(N-Pyridyl)-1,3,4-oxadiazoles |

(a) In combination with $ClO_2$ treatment for bacteria control.

(b) Aqueous HCl

(c) 0.1 to 6% with antifreezers such as glycols.

(d) Gas stream containing $H_2S$ or $CO_2$

(e) Forms a film of iron disulfide

(f) Relatively nontoxic, substitution of chromate-based corrosion inhibitors, conventional phosphate, and organophonphonate inhibitors and the zinc-based inhibitors

(g) $CO_2$ environment

(h) Calcium choloride brine

(i) 10 – 500 ppm

(j) 5 – 200 ppm to inhibit naphthenic acid corrosion

(k) In drilling equipment

(41) Oilfield Chemicals, Johannes Karl Fink, Gulf Professional Publishing, Amsterdam, pg. 102, 2003,

Scale Inhibitors

Some risk of scale deposition occurs in many operations in the petroleum industry.  Scale deposition happens particularly in production, stimulation, and transport.  Scaling can occur when a solution becomes supersaturated, which occurs mostly if the temperature changes in the course of injection operations.  Also, if two chemicals that will form a precipitate are brought together, a scale is formed.  From a thermodynamic perspective, there is a stable region, a metastable region, and an unstable region, separated by a binodale curve and the spinodal curve, respectively.

The scale may consist of calcium carbonate, barium sulfate, gypsum, strontium sulfate, iron carbonate, iron oxides, iron sulfides, and magnesium salts. (42)

The operating premise behind scale inhibition is to prevent scale deposition.  Scale inhibition can be achieved either by adding substances that react with potential scale-forming substances so that from a thermodynamics standpoint the stable region is reached or by adding substances that suppress crystal growth.

Conventional scale inhibitors are hydrophilic, that is, they dissolve in water.  In the case of down-hole squeezing, it is desirable that the scale inhibitor is adsorbed on the rock to avoid washing out the chemical before it can act as desired.  However, adsorption on the rock may change the surface tension and the wettability of the system.  To overcome these disadvantages, oil-soluble scale inhibitors have been developed.  Coated inhibitors are also available.  Often, scale inhibitors are not applied as such, but rather in combination with corrosion inhibitors.

Thermodynamic inhibitors are complexing and chelating agents, suitable for specific scales.  For example, for scale inhibition of barium sulfate, common chemicals are ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid.  The solubility of calcium carbonate can be influenced by varying the pH or the partial pressure of carbon dioxide.  The solubility increases with decreasing pH and increasing partial pressure of $CO_2$, and it decreases with temperature.

However, usually the solubility increases with higher temperature.  The temperature coefficient of solubility is dependent on the enthalpy of dissolution.  An exothermic enthalpy of dissolution causes a decrease in solubility with increased temperature, and vice versa.

Kinetic inhibitors for hydrate formation may also be effective in preventing scale deposition. (43)  This may be understood in terms of stereospecific and nonspecifice mechanisms of scale inhibition.

Another mechanism of scale inhibition is based on adherence inhibitors.  Some chemicals simply suppress the adherence of crystals to the metal surfaces.  These are surface-active agents.

Both inorganic acids, such as hydrochloric acid and hydrofluoric acid, and organic acids, such as formic acid, can be used to decrease pH.  Acids are used in combination with surfactants. Various phosphates, pyrophosphates, polyphosphates, and metaphosphates belong to the phosphate type of scale inhibitors.  Of course, the classic ethylenediaminetetraacetic acid (EDTA) shows chelating properties, and there are various organic multifunctional acids and hydroxyacids.

(42) R.W.Keatch. Removal of sulphate scale from surface.  Patent: GB 2314865,1998.
(43) C.S.Sikes and A.Wierzbicki. Stereospecific and nonspecific inhibition of mineral scale and ice formation.  In *Proceedings Volume*. 51st Annu NACE Int Corrosion Conf (Corrosion 96) (Denver, CO, 3/24-3/29), 1996.

Conventional polymer and phosphonate scale inhibitors may not be appropriate for application in high-pressure and high-temperature reservoirs.  Only a limited range of commercially available oil field scale inhibitor chemicals are sufficiently thermally stable at temperatures above 150°C.  These chemicals are homopolymers of vinyl sulfonate and copolymers of acrylic acid and vinyl sulfonate.  Other polymers, such as polymaleic acid, polyitaconic acid, and maleic acid/acrylic acid copolymers, may offer similar thermal stability.  However, they are not available (as of 1995) from oil field chemical suppliers. (44) Thermal stability tests, influence on pH, ionic strength, and oxygen on conventional polymer and phosphonate scale inhibitors along with phosphinopolycarboxylate, polyvinyl sulfonate, penta-phosphonate, and hexa-phosphonate have confirmed their effectiveness. (45)

Scale Inhibitors

| | |
|---|---|
| 1-Hydroxyethylidene-1, 1-disphosphonic acid | Carboxymethylinulin |
| Carbonic dihydrazide, $H_2NNHCONHNH_2$ | Polycarboxylic acid salts |
| Polyaminealkylphosphonic acid and carboxymethylcellulose or polyacrylamide | Phosphoric acid esters or rice bran extract |
| Polyacrylic acid and chromium | Poly(phosphino maleic anhydride) |
| Polyacrylates (a) | N,N-Diallyl-N-alkyl-N-(sulfoalkyl) ammonium betaine copolymer (with N-vinyl pyrrolidone or acrylamide), diallylmethyltaurine hydrochloride ($CH_2=CH-CH_2CL$ X $CH_3-HN-CH_2-CH_2-SO_3Na$) |
| Amine methylene phosphonate (b) | Aminotri(methylenephosphonic acid) |
| Phosphonomethylated polyamine | Polyaspartates |
| Oil soluble | Polyacrolein |
| Sulfonated polyacrylate copolymer | Naphthylamine polycarboxylic acids |
| Tetrakis-hydroxymethyl-phosphonium sulfate | Phosphonic acid and hydrofluoric acid |
| Phosphonates | Tertiary amines (c) |

(a) In borate crosslinked fracturing fluids
(b) High temperature
(c) Oil soluble

(44) I.R.Collins. Scale inhibition at high reservoir temperatures. In *Proceedings Volume*. IBC Tech Serv Ltd Advances in Solving Oilfield Scaling Int Conf (Aberdeen, Scotland, 11/20-11/21), 1995.
(45) S.J.Dyer, G.M.Graham, and K.S. Sorbie. Factors affecting the thermal stability of conventional scale inhibitors for application in high pressure/high temperature reservoirs. In Proceedings Volume, pages 167-177. SPE Oilfield Chem Int Symp (Houston TX, 216-2/19), 1999.

Gelling Agents

Organic and inorganic gels are used to seal formations with high permeability. Sealing can be permanent or temporary.  In this way, undesirable flows in the formation can be suppressed.  Gelling agents are mainly used for water shutoff and limiting sand production; some agents can be used also for primary plugging of surface and flow strings, as well as for eliminating lost circulation. (46)  However, the high prices often limit wide applications.

Flow-deflecting technologies based on gel-forming agents are effective in highly water-invaded multizone reservoirs.  Redistribution of the flow is achieved by equalizing the injectivity profile of the injection wells and reducing the content of produced water in the producing wells. Redistibution also reduces the consumption of electricity, demulsifiers, and fuels used for oil treating in the field.  To broaden the use of gel technologies, it is necessary to solve certain problems of developing and manufacturing mobile units for preparing and injecting large volumes of gel compositions in wells and for producing nonfreezing agents for year-round stimulation treatments. (47) (See Chart M-3 Appendix)

The formation of gels can be achieved by various chemical principles:
> 1. Bringing polyanionic and polycationic substances together
> 2. Physical crosslinking of carboxyl-functional polymers with multivalent ions.
> 3. Using chelating agents

Commonly used salts, crosslinkers, and chelating agents:
> 1. Aluminum citrate
> 2. Chromium sulfate
> 3. Ferrochromo-lignosulfonate
> 4. Manganese nitrate
> 5. Potassium bichromate
> 6. Sodium bichromate
> 7. Ferric acetylacetonate
> 8. Ammonium ferric oxalate

(46) S.A.Ryabokon and V.V.Goldshtein. Prospects of developing polymer plugging agents. *Neft Khoz*, (5):7-13, May 1989.
(47) B.M.Gustov, A.M.Khatmullin, V.S.Asmolovskii, V.G.Zyurin, F.Kh.Saifutdinov, and L.E.Lenchenkova.  Field tests of gel technologies at the Arlan field. *Neft Khoz*, (2):36-38, February 1996.

**Chapter 4: Overall Outcomes**

**Transport**

Pipelines have a long history.  In ancient times, pipelines were used for water transport.  Examples are still visible in archaeologic areas.  However, it is clear that these early constructions could not bear large pressures.  The advent of gas pipelines started between 1820 and 1830 with the distribution of town gas.  Currently pipelines are indispensable in petroleum industries for the transport of various materials, including natural gas, crude oil of various types, and refined products. This section will now detail the additives and chemicals that facilitate the transport of fossil fuel products.

Certain requirements concerning the purity of the product to be transported must be fulfilled.  For natural gas, the water content should be kept below a certain level to reduce hydrate formation.  In addition, oxygen and sulfur must be controlled effectively.

Main Classes of Additives and Chemicals Used for Transport

| Additive | Remarks |
|---|---|
| Drag reducers | For both liquid and gas transport |
| Pour-point depressants | Reduce pour points of waxy crudes |
| Odorizing additives | For safety |
| Gas hydrate inhibitors | For gas and multi-phase transport to prevent hydrate deposits |
| Surfactants | For multiphase transport of heavy crudes |
| Corrosion Inhibitors | Both chemical inhibitors and biocides |
| Paraffin Inhibitors | Prevent paraffin depositions |

Methods used to control presumptive corrosion include deaeration and dehydration.  Carbon dioxide and hydrogen sulfide are the main corrosives in pipelines for natural gas, but they are only aggressive in the presence of water.  Therefore sweetening and drying the gas are useful to prevent corrosion.  In oil pipelines, water emulsified in crude oil can cause serious corrosion problems. [48] Emulsified crude oil in separated produced water is also an environmental and disposal problem.

Natural gas consists mainly of methane although there are trace amounts of higher hydrocarbons, nitrogen, and even helium.  It is typical in the gas transportation and storage industry to try to strip out higher hydrocarbons such as ethane, propane, butane, and unsaturated hydrocarbons from natural gas if the gas is to be transmitted through pipelines.  This leaves mostly methane (with some traces of nitrogen and carbon dioxide) to be transported by the gas pipeline.  The materials that are stripped out are then transported or stored separately, often as liquids.

The compressibility factor $z$ of methane is always less than 1.0 in normal temperature ranges (i.e., between -40° and 50°C).  Furthermore, the compressibility factor decreases as the pressure rises or the temperature falls.

[48] M.J.Bromley, S.H.Gaffney, and G.E.Jackson.  Oilfield emulsion control, techniques and chemicals used to separate oil and water. In Proceedings Volume, volume 3. Inst Corrosion UK (Corrosion 91) Conf (Manchester, England,10/22-10/24), 1991.

Therefore, less energy is needed to pump a given volume of methane (measured at standard volume) at any given normal temperature than would be expected at that temperature if the methane were an ideal gas. This effect is more marked at higher pressures. Similarly, as the pressure is increased at a constant temperature, more methane (measured at standard volume) can be stored in a given volume than would be predicted from the ideal equation.

Below 7MPa, the dominant variable for the compressibility factor in the PVY equation is the molecular weight of the gas. At this pressure level, the addition of ethane or propane increases the molecular weight of the gas more rapidly than the $z$ factor decreases. Thus there is an advantage to removing ethane, propane, etc. from the gas.

At pressures greater than 7MPa it is advantageous to add substances such as $C_2$ or $C_3$ hydrocarbon compound, carbon monoxide, hydrogen fluoride, ammonia, or a mixture of these with the natural gas. Ammonia without other additives is useful as an additive for gas storage at pressures down to about 5.5MPa. Above a lower limit, which varies with the additive being added and the pressure, this results in a smaller $M_w \times z$ product, and therefore a decrease in the amount of power needed to compress the mixture for storage and to keep it compressed. It is also advantageous to add ammonia to natural gas to be transmitted through pipelines at pressures above 5.5MPa. Depending on the cost, it also can be advantageous to add carbon monoxide. Hydrogen fluoride is also effective, but is prohibitive because of the toxicity and corrosive properties. The precise amount of each additive that can be added at any pressure for beneficial results can be found by calculation the product of the molecular weight times the $z$ factor of the resulting mixture $M_w \times z$, and comparing it with the product of the molecular weight times the $z$ factor of the original natural gas. If the product $M_w \times z$ is smaller for the mixture than for the natural gas, energy can be saved in pumping and compression. (49)

The use of two or more additives has a synergestic effect in many cases, so that an even smaller amount of each is needed than would be if only one were present to produce the $z$ factor over that of an equivalent standard volume of natural gas at the pressure and temperature involved.

When the mixture is pumped through a pipeline, however, an additional effect with ammonia emerges. In a pipeline, there are pumping stations at intervals along the pipeline. At each pumping station, the gas is compressed. As the gas moves toward the next pumping station, it gradually loses pressure and expands. The compression during passage through the compressor station heats the gas; the gas cools while passing through the pipeline, transferring some of its heat to the surrounding soil through the pipeline wall. Ammonia has the property of being a refrigerant, which absorbs heat as it expands. Thus when an ammonia-natural gas mixture is compressed and then is subsequently allowed to flow through a gas pipeline, the ammonia cools the mixture as it expands. This is regarded as an additional advantage. (50)

If refined products, such as gasoline, diesel, jet fuel, or kerosene, are transported in a pipeline, where otherwise sour hydrocarbon fluids are transported, there may be an undesired enrichment of sulfur in the refined products. This can be avoided if the oxygen level of the transportant is maintained at below 20 ppm. (51)

(49) I. Morris and G. Perry. Pipeline transmission method. Patent: US 6201163, 2001.
(50) I. Morris and G. Perry. High pressure storage and transport of natural gas containing added $C_2$ or $C_3$, or ammonia, hydrogen fluoride or carbon monoxide. Patent: US 6217626, 2001.
(51) R.J.Falkiner and M.A.Poirier. Method for reducing elemental sulfur pick-up by hydrocarbon fluids in a pipeline. Patent: CA 2158789, 1996.

A gas containing entrained asphaltene-containing hydrocarbons is conditioned for pipeline transportation by injecting a surface active compound that is composed of a mixture of demulsifying agent, antifoaming agent, a dispersant, aromatic solvent, and alcohol solvent, whereby the formation of emulsion from asphaltene-containing hydrocarbons is prevented. (52)

Heavy Crudes

The most relevant parameters in pipeline transportation of heavy crude oil are velocity, viscosity, temperature, density, and pour point. (53) Heavy crude can be transported on trunk systems in a variety of modes, including segregation, blending, and batching. Segregation requires separate pipelines, blending consists of mixing crudes, and batching refers to shipping crude in discrete batches. There are a number of methods for enhancing the transportatibility of heavy crude. These include oil-in-water emulsion formation, droplet suspension, dilution, the use of drag-reducing additives, and heating.

Corrosion Control

Coatings, cathodic protection, and chemical additives are used extensively to prevent internal and external pipeline corrosion. The excessive use of incompatible chemical additives has caused severe problems in gas-transporting systems. Costs arising from these problems often exceed the costs of the chemicals themselves. The careful evaluation and selection of chemical additives can minimize these problems and reduce operating costs. (54)

Inhibitors may be classified according to their solution properties as either oil-soluble inhibitors, water-soluble inhibitors, or dispersible inhibitors. Chemical inhibitors act as film formers to protect the surface of the pipeline. Corrosion inhibitors, used for the protection of oil pipelines, are often complex mixtures. The majority of inhibitors used in oil production systems are nitrogenous. The listing of such is as follows:

Amides or inidazolines, salts of nitrogenous molecules with carboxylic acids (fatty acids, napthenic acids), nitrogen quaternaries, polyoxylated amines, amides, and imidazolines, and nitrogen heterocyclics.

One problematic and frequent factor in oil transport is that of paraffin deposition and accumulation on the interior walls of the transport media. The techniques used to remove and prevent this type of deposition have been discussed thoroughly by the Southwestern Petroleum Association. (55)

(52) A.L.Mendoza. Surface active composition for conditioning a gas containing entrained asphaltenes. Patent: GB 2279964, 1995.

(53) J.M.Gerez and A.R.Pick. Heavy oil transportation by pipeline. In *Proceedings Volume*, volume 2, pages 699-710. 1st ASME et al Int Pipeline Conf (Calgary, Canada, 6/9-3/13), 1996.

(54) Y.Wu. Chemical problems and costs involved in downstream gas systems. In *Proceedings Volume*. NACE Int Corrosion Forum (Corrosion 90) (Las Vegas, NV, 4/23-4/27), 1990.

(55) L.R.Heinze, N.Shahreyar, and B.M.Baruah. A review of past 50 years of paraffin prevention and removal techniques as presented in the SWPSC (Southwestern Petroleum Short Course). In Proceedings Volume, pg.230-238. 48th Annu Southwestern Petrol Short Course Assoc Inc et al Mtg(Lubbock, TX,4/25-4/26,2001)

In particular, inhibitors for paraffin deposits are copolymers of ethylene with vinyl acetate(56), or polymers from p-nonylphenylmethacrylate and p-dodecylphenyl methacryalte(57).  These materials lower the pour point of the oil.  It has been shown that for oils which differ in the content of n-paraffins and asphalt-resinous substances, it is necessary to use blends of copolymers of different compositions and molecular weights to obtain optimal efficiency.  Polyacrylamide and wastes from the production of glycerol with a concentration of 40 mg/l if oil have also been claimed to be effective as paraffin inhibitors.

In waxy crudes, the wax has a tendency to become deposited during storage of the crude oil in tanks or while flowing through pipelines.  The deposition in the pipeline severely affects the pipeline throughput.  The deposits have to be removed periodically from the storage tanks and pipelines by pigging operations.

The wax deposition behaviors of Bombay high crude oil have been studied under different conditions using a cold disk-type assembly(58). It is observed that the deposition occurs much less with additive-treated crude than with untreated crude under otherwise identical conditions.  However, the deposits obtained from treated crude have slightly higher melting points and less oil content. The wax separation temperature of crude oils can be determined from their viscosity behavior. (59)

Drag Reducers

Pipeline flow improvers, or drag-reducing agents, have been utilized in the petroleum industry for many years(60).  The first application of drag reducers in the petroleum industry was to reduce the down-hole pressure loss during the pumping of fluids down-hole to fracture-tight formations.  One of the first large scale pipeline applications was to increase the throughput of crude oil on the Trans-Alaskan pipeline in 1979.  Because of the reduction of the apparent viscosity, drag reducers are useful for saving energy required for pumping.

Drag reduction on gas transmission lines can be achieved by applying a thin chemical coating on the pipe's inner surface to reduce friction between the flowing gas and pipe wall.  An important criterion for gas drag reduction is that the additive can bond strongly onto metal surfaces and form a smooth film to mitigate the turbulence at the gas-solid interface(61).  Effective gas drag reducers have properties similar to corrosion inhibitors, lubricants, and surfactants.  Fatty acid amines or amides exhibit these properties.

(56) A.G.Sharov, R.A.Terteryan, L.I.Burova, and L.A.Shulgaitser.  Effect of compolymer inhibitor of paraffin deposits on oils of various fields. Neft Khoz, (9):55-58 September 1989.

(57) S.Handa, P.K.G.Hodgson, and W.J.Ferguson. Asphaltene precipitation inhibiting polymer for use in oils. Patent:GB 2337522, 1999.

(58) M.S.Hameed, E.J.Taha, and M.M.F.Al-Jarrah.  Observations on the effect of low molecular weight polyethylene-oxides on the flow of water in closed pipes and standard fittings. *J Petrol Res*, 8(1):47-60, June 1989.

(59) H.U.Khan, J.Handoo, K.M.Agrawal, and G.C.Joshi. Determinaion of wax separation temperature of crude oils from their viscosity behavior. Erdol Erdgas Kohle, 107(1):21-22, January 1991.

(60) N.E.Almond. Pipeline flow improvers. In *Proceedings Volume*, pages 307-311. API Pipeline Conf (Dallas, TX, 4/17-4/18), 1989.

(61) Y.H.Li, G.R.Chesnut, R.D.Richmond, G.L.Beer, and V.P.Caldarera. Laboratory tests and field implementation of gas drag reduction chemicals. In Proceeding Vol, pg. 457-469. SPE Oilfield Chem Int Symp (Houston,TX,2/18-2/21), 1997

Drag reducing additives are important in oil drilling applications and the maintenance of pumping equipment in pipelines. Flow drag in pipes can be reduced by adding a small amount of high-molecular polymer. Pipeline flow improvers, or drag-reducing agents (DRAs), have been utilized in the petroleum industry for many years. The first application of drag reducers was the use of guar in oil well fracturing, presently a routine practice. The quantities of DRA used in this application were very large. Part of the reason for the increased use of DRA is an economic factor, namely, to offset power costs. The DRA cost for moving an additional barrel of product through a pipeline system can be less than $0.05/bbl. This cost level has been made possible by improved performance in commercially available DRAs and a nearly unchanging price structure.

      Drag reduction occurs by the interactions between elastic macromolecules and turbulent-flow macrostructures. In turbulent pipe flow, the region near the wall, composed of viscous sublayer and a buffer layer, plays a major role in drag reduction.

      The most serious problem in the effectiveness of drag reducers is the chain degradation of polymers by shear strains in turbulent flow. Ultra-high-molecular-weight polymers are more susceptible to shear-induced degradation(62). Polymers with linear-chain structures are more vulnerable than branched polymers(63) and natural gums with semi-rigid structures. The mechanism of shear degradation is assumed to be associated with chain elongation. The chain degradation is often observed when the shear rate is increased to a critical point, after which drag reduction sharply decreases.

      The friction drag and heat-transfer-reduction phenomena associated with turbulent flows of so-called drag-reducing fluids are not well understood(64). It is believed that elastic fluid properties are strongly related to these phenomena. However, not all drag-reducing fluids are viscoelastic, nor are all viscoelastic fluids drag reducing, suggesting that drag reduction and viscoelasticity are probable incidentally-accompanying phenomena. It is argued that turbulence suppression (i.e., flow laminarization) is a determining factor for the reduction phenomena—not the fluid elasticity—because of the flow-induced anisotropic fluid structure and the associated properties, whereas the fluid elasticity may be a major cause for the laminar heat-transfer augmentation.

Copolymers of ά-Olefins and Others Used as Drag Reducers

| | |
|---|---|
| Divinylbenzene/1-hexene,1-octene,1-decene, and 1-dodecene  (a) | C12 to C18 acryalte or methacrylate/ionic monomer  (e) |
| Styrene/N-vinylpyridine | Tert-Butlystyrene/alkyl acrylate, acrylic acid or methacrylic acid |
| Ethene(ά-Olefins)  (b) | Acrylamide-acrylate |
| Homo- or co-polymers that ά-Olefins  (c) | Ultrahigh-molecular-weight polyolefin |
| Polyisobutene  (d) | Styrene/methyl styrene sulfonate/N-vinylpyridine (NVP)  (f) |
| (Meth) acrylic acid esters | |

(a) Synthesis by a Ziegler-Natta process   (b) Up to C30, Ziegler-Natta.  (c) Molecular weight of up to 15,000 and an isotacticity of 75% or greater  (d) Oil-soluble polymer  (e) Reduce friction in the flow of a hydrocarbon fluid by a factor of 5 at concentrations low as 1 to 25 ppm.    (f) Polyampholytes.

(62) B.Gampert and P.Wagner. *The influence of polymer additives on velocity and temperature fluid*, page 71. Springer-Verlag, Berlin, Germany, 1985.
(63) H.F.D. Chang and J.S.Meng. *Physichochem Hydrodyn*, 9:33, 1987
(64) M.Kostic. On turbulent drag and heat transfer reduction phenomena and laminar heat transfer enhancement in non-circular duct flow of certain non-Newtonian fluids. *Int J Heat Mass Transfer*; 37:133-147, March 1994.

**Antifreeze Agents**

An antifreeze is defined as an additive that, when added to a water-based fluid, will reduce the freezing point of the mixture(65). Antifreezes are used in mechanical equipment in environments below the freezing point to prevent the freezing of heat-transfer fluids. Another field of application is in cementing jobs to allow operation below the freezing point.

Freezing point depression follows the colligative laws of thermodynamics at low concentrations added to water. At the same time the boiling point generally will be increased. The freezing point depression can be readily explained from the theory of phase equilibria in thermodynamics.

In equilbrium the chemical potential must be equal in coexisting phases. The assumption is that the solid phase must consist of one component, water, whereas the liquid phase will be a mixture of water and salt. So the chemical potential for water in the solid phase $\mu_s$ is the chemical potential of the pure substance. However, in the liquid phase the water is diluted with the salt. Therefore the chemical potential of the water in liquid state must be corrected. $x$ refers to the mole fraction of the solute, that is, salt or an organic substance. The equation is valid for small amounts of salt or additives in general:

$$\mu_s = \mu_1 + RT \ln(1-x)$$

$$\frac{\mu_s - \mu_1}{RT} = \ln(1-x) = -x$$

The derivative with respect to temperature will give the dependence of equilibrium concentration on temperature itself:

$$\frac{d \frac{\mu_s - \mu_1}{RT}}{dT} = \frac{-dx}{dT} = \frac{\Delta H}{RT^2}$$

$\Delta H$ is the heat of melting of water. Because the heat of melting is always positive, an increase of solute will result in a depression of the freezing point. For small freezing point depressions, the temperature on the right-hand side of the equation is treated as a constant. Furthermore, it is seen that additives with small molecular weight will be more effective in depressing the freezing point. Once more it should be noted that the preceding equation is valid only for small amounts of additive. Higher amounts of additive require modifications of the equation; in particular, the concept of activity coefficient has to be introduced. The phase diagram over a broader range of concentration can be explained by this concept.

The classic antifreeze agents in heat-transfer liquids are brine solutions and alcohols. Human toxicity and aquatic toxicity have been measured typically with fresh formulations only. Spent fluids may contain various contaminants and degradation products that may change the toxic effects.

(65) B.A.Stefl and K.L.George. Antifreezes and deicing fluids. In *Kirk-Othmer*, Encyclopedia of Chemical Technology, vol3, pg.347-366. J.Wiley& Sons,1996. 1996.

The toxicity of antifreeze agents is mainly due to the main ingredient, ethylene glycol. It is often believed that glycols are healthy to the skin, because the compounds are related to glycerol. This is completely wrong, because the degradation metabolism is completely different due to the difference of a single carbon atom.

Ethylene glycol is acutely toxic to humans and animals if ingested. Ethylene glycol is defined as an animal teratogenic(66). Propylene glycol has not shown teratogenic effects, and the oral toxicity is lower. On the other hand, propylene glycol is more irritating to the skin than ethylene glycol.

The aquatic toxicity of antifreeze agents is not strictly a function of the main component. Aquatic toxicity may come also form minor components in the formulation. both ethylene glycol and propylene glycol are believed to be essentially nontoxic to aquatic life.

Recycling is achieved either by simply filtering or by redistillation. In the case of filtering, only deposits are removed. There is essentially no information concerning the activity of other additives as corrosion inhibitors. Redistillation is more effective because this process recovers the glycol in high quality, although it is more complicated and cost intensive than filtering. The refined glycol must be re-inhibited before use. Spent antifreeze formulations can be purified before recycling. If antifreeze is kept separate form waste oils, it can be easily treated and recycled into a new product.

Mixtures of aqueous emulsions of oil can be more effectively transported through pipelines if certain antifreeze formulations are added to the system. Stable oil-in-water emulsions for pipeline transmission by using 0.05% to 4.0% ethoxylated alkylphenol as an emulgator and a freezing point depressant for water enable pipeline transmission at temperatures below the freezing point of water. (67)

Highly viscous petroleum oil containing 30% to 80% water can be transported through pipes more efficiently when a 1:1 mixture of washing liquid and antifreeze (i.e. ethylene glycol with a surfactant) is added to the oil in amounts of 0.002% to 0.2% by weight. In addition to increased efficiency of transport, reduced corrosion of pipes can be achieved. (68)

Antifreeze agents are occassionally added to reduce the freezing point of the drilling fluid itself(69). Such a water-based drilling fluid is composed of water, clay or polymer, and a poly-glycerol. The drilling fluid is useful in low-temperature drilling.

(66) http://www.thefreedictionary.com/teratogenic  adj: of or relating to substances that can interfere with normal embryonic development.

(67) A.A.Gregoli and A.M.Olah.  Low-temperature pipeline emulsion transportation enhancement. Patent: US 5156652, 1992.

(68) V.I.Ivashov, R.U. Shafiev, T.Azizkhanov, K.Kh.Azizov, and M.A.Usmanova. Transporting highly viscous, water-laden oil through pipe—comprises addition to oil of 1:1 mixture of washing liquid and prescribed antifreeze (rus). Patent: SU 1827499-A, 1993.

(69) A.H.Hale, G.C.Blytas, and A.K.R.Dewan.  Water base drilling fluid. Patent: GB 2216574, 1989.

## Chapter 5: Analysis

**Enhanced Oil Recovery**

Approximately 60% to 70% of the oil in place cannot be produced by conventional methods(70). Enhanced oil-recovery methods gain importance in particular with respect to the limited worldwide resources of crude oil. The estimated worldwide production from enhanced oil-recovery projects and heavy-oil projects at the beginning of 1996 was approximately 2.2 million barrels per day (bpd). This is approximately 3.6% of the world's oil production. At the beginning of 1994, the production had been 1.9 million bpd. (71)

Enhanced oil-recovery processes include chemical and gas floods, steam combustion, and electric heating. Gas floods, including immiscible and miscible processes, are usually defined by injected fluids (carbon dioxide, flue gas, nitrogen, or hydrocarbon). Combustion technologies can be subdivided into those that autoignite and those that require a heat source at injectors. (72)

Chemical floods are identified by the chemical type that is injected. The most common processes are polymers, surfactants, and alkalis, but chemicals are often combined. For example, polymer slugs usually follow surfactant or alkaline slugs to improve sweep efficiency. Injection of materials that plug permeable channels may be required for injection profile control and to prevent or mitigate premature water or gas breakthrough. Crosslinked or gelled polymers are pumped into injectors or producers for water shutoff or fluid diversion. Cement squeezes often can effectively fix near-wellbore water channeling problems. The design of chemical injection-enhanced oil recovery projects can be more complicated than that of waterflood projects. Down-hole conditions are more severe than are those for primary or secondary recovery production. Well injectivity is complicated by chemicals in injected waters, so in addition to precautions used in waterfloods, chemical interactions, reduced injectivity, deleterious mixtures at producers, potential for accelerated corrosion, and possible well stimulations to counter reduced injectivity must be considered.

The two most common types of enhanced oil recovery techniques used in the lower great plains area of the continental United States are (1) waterflooding and (2) carbon dioxide flooding. There are many other types of recovery techniques available; however, for clarity and application to the author's current geographical region, only the two aforementioned will be considered in detail.

The following table presents the common surfactants used in combination with current waterflood procedures. Commercial alkene sulfonates are a mixture of alkene sulfonate, hydroxyalkane sulfonate, and olefin disulfonate. (73)

(70) A.H. Al-Khafaji. Implementations of enhanced oil recovery techniques in the Arab world are questioned. In *Proceedings Volume*, pages 124-133. 6th Int Energy Found et al Mediter Petrol Conf (Tripoli, Libya, 11/23-11/25), 1999.
(71) G.Moritis. EOR Survey and analysis. *Oil Gas J*, 94(16):49-77, 1998.
(72) G. Duncan. Enhanced recovery engineering: Pt 1. *World Oil*, 215(9):95, 97-100, September 1994.
(73) J.K.Borchardt and A.R.Strycker. Olefin sulfonates for high temperature steam mobility control: Structure-property correlations. In *Proceedings Volume*, pages 91 -102. SPE Oilfield Chem Int Symp (Houston TX, 2/18-2/21), 1997.

Surfactants for Waterflooding

| | |
|---|---|
| Ethoxylated methylcarboxylates | Alkyl xylene sulfonates, polyethoxylated alkyl phenols, octaethylene glycol mono n-decyl ether, and tetradecyl trimethyl ammonium chloride |
| Propoxyethoxy glyceryl sulfonate | Anionic sodium dodecyl sulfate (SDS), cationic tetradecyl trimethyl ammonium chloride (TTAC), nonionic pentadecylethoxylated nonylphenol (NP-15), and nonionic octaethylene glycol N-dodecyl ether |
| Alkylpropoxyethoxy sulfate as surfactant, xanthan, and a copolymer of acrylamide and sodium 2-acrylamido-2-methylpropane sulfonate | Dimethylalkylamine oxides as cosurfactants and viscosifiers |
| Carboxymethylated ethoxylated surfactants (CME) | (N-Dodecyl)trimethylammonium bromide |
| Polyethylene glycols, propoxylated/ethoxylated alkyl sulfates | Petrochemical sulfonate and propane sulfonate of an ethoxylated alcohol or phenol |
| Mixtures of sulfonates and nonionic alcohols | Petrochemical sulfonate and α-olefin sulfonate |
| Combination of lignosulfonates and fatty amines | |

Combination flooding comprises the combination of at least two basic techniques form gas flooding, caustic flooding, surfactant flooding, polymer flooding, and foam flooding. There may be synergisms between the various chemical reagents used. There are specific terms that clarify the individual combination of the basic methods, such as surfactant-enhanced alkaline flooding, alkaline-assisted thermal oil recovery, and others.

Carbon Dioxide Flooding

In the 1990s certain research groups focused on the development of $CO_2$-soluble polymers usable as direct thickeners, in particular, ionomers. (74)
Sandstone rock surfaces are normally highly water-wet. These surfaces can be altered by treatment with solutions of chemical surfactants or by asphaltenes. Increasing the pH of the chemical treating solution decreases the water wettability of the sandstone surface and, in some cases, makes the surface medium oil-wet(75). Thus the chemical treatment of sandstone cores can increase the oil production when flooded with carbon dioxide.

(74) F.S.Kovarik and J.P.Heller. Improvement of CO2 flood performance. US DOE Rep DOE/Mc/21136-24, New Mex Inst Mining Techn, August 1990.
(75) D.H.Smith and J.R.Comberiati. Chemical alteration of the rock surfaces by asphaltenes or surfactants, and its effect on oil recovery by CO2 flooding. In *Proceedings Volume*. Annu AICHE Mtg (Chicago, IL,11/11-11/16), 1990.

A cosolvent used as a miscible additive to $CO_2$ changed the properties of the supercritical gas phase. The addition of a cosolvent resulted in increased viscosity and density of the gas mixtures and enhanced extraction of the oil compounds into the $CO_2$-rich phase. Gas phase properties were measured in an equilibrium cell with a capillary viscometer and a high-pressure densitometer. Cosolvent miscibility with $CO_2$, brine solubility, cosolvent volatility, and relative quantity of the cosolvent partitioning into the oil phase are factors that must be considered for the successful application of cosolvents. The results indicate that lower-molecular-weight additives, such as propane, are the most effective cosolvents to increase oil recovery. (76)

By adding common solvents as chemical modifiers, the flooding fluid shows marked improvement in solvency for heavy components of crudes because of its increased density and polarity. (77) Miscible or immiscible carbon dioxide injection is considered to be one of the most effective technologies to improve oil recovery from complicated formations and hard-to-recover oil reserves. Application of this technology can increase ultimate oil recovery by 10% to 15%. One of the main advantages of this technology is that it can be applied in a wide range of geologic conditions for producing both light and heavy oils.

The main factors restraining wide application of $CO_2$ flooding are the dependence on natural $CO_2$ sources, transportation of $CO_2$, safety and environmental problems, breakthrough of $CO_2$ to the production wells, and corrosion of well and field equipment. This restrains the wide implementation of $CO_2$ injection technology, not only in many European countries, but also worldwide, where this technology could significantly improve oil production and ultimate oil recovery from depleted oil formations. Another technology for in situ $CO_2$ generation has been developed and described. It is based on an exothermic chemical reaction between gas-forming water solution and low-concentration active acids. (78)

Hydrocarbons and other fluids are recovered at a production well by a mixture of $CO_2$ and 0.1% to 20% by weight trichloroethane at a temperature and pressure above the bubble point of the mixture, which ensures that the mixture will be in a single phase. (79)

When the temperature of a carbonate reservoir that is saturated with high-viscosity oil and water increases to 200°C or more, chemical reactions occur in the formation, resulting in the formation of considerable amounts of $CO_2$. The generation of $CO_2$ during thermal stimulation of a carbonate reservoir results from the dealkylation of aromatic hydrocarbons in the presence of water vapor, catalytic conversion of hydrocarbons by water vapor, and oxidation of organic materials. Clay material and metals of variable valence (e.g., nickel, cobalt, iron) in the carbonate rock can serve as the catalyst. An optimal amount of $CO_2$ exists for which maximal oil recovery is achieved. The performance of a steamflooding process can be improved by the addition of $CO_2$ or methane.

(76) C.Raible. Improvement in oil recovery using cosolvents with CO2 gas floods. US DOE Fossil Energy Rep NIPER-559, NIPER, January 1992.

(77) R.J.Hwang and J.Oritz. Mitigation of asphaltics deposition during CO2 flood by enhancing CO2 solvency with chemical modifiers. *Organic Geochem*, 31(12):1451-1462, 1999.

(78) I.S.Dzhafarov, S.V.Brezitsky, A.K.Shakhverdiev, G.M.Panakhov, and B.A. Suleimanov. New in-situ carbon dioxide generation enhanced oil recovery technology. In *Proceedings Volume*, number 106. 10th EAGE Impr Oil Recovery Europe Symp (Brighton, UK, 8/18-8/20), 1999.

(79) J.J.C.Hsu. Recovering hydrocarbons with a mixture of carbon dioxide and trichloroethane. Patent:US 5117907, 1992.

Low-Permeability Flooding

       Oil recovery form diatomaceous formations is usually quite limited because a significant portion of oil saturation may be bypassed using conventional production techniques such as primary, waterflooding, cyclic or drive steaming.  Significant improvement of oil recovery would require that a method of displacing oil from the interior of the diatoms into the flow channels between the diatoms be provided. Furthermore, it would be necessary to improve permeability in the natural flow channels so that the oil can be recovered.  A combination of chemical additives is used to increase water wetness of a rock thereby increasing the capillary pressure which forces oil and water from the diatomaceous formation. These chemical additives include wetting agents (e.g.,mono-,di-, tri-basic forms of sodium or potassium phosphate, and sodium silicate) and surfactants.  These surfactants can be either sulfonates, ammonium salts of linear alcohol, ethoxy sulfates, or calcium phenol ethoxylated alkyl sulfonates.  These surfactants lower the interfacial tension between oil and water thereby allowing oil to flow more freely through the diatomaceous matrix.  Imbibition experiments with up to 3% by weight of active surfactant concentration indicate a 31% improvement in oil recovery over that obtainable with brine alone. (80)

Tracers

       The addition of tracer chemicals to an injection fluid provides information on the permeability of a reservoir.  Small amounts of a tracer are added to the injected fluid and the distribution of a tracer at the production well is monitored with respect to time.  Radioactive tracers and nonradioactive tracers exist.

       Isotope-labeled tracers behave like the components in the fluid of interest.  For example, tritium water behaves like water.  If less similar chemicals are used as tracers, selective adsorption, chemical reaction, and liquid-liquid distribution must be considered.  The tracer must be chosen so that the analytic method is sufficiently sensitive to detect the tracer in the desired amounts.

       Tritiated or $^{14}$C-tagged hydrocarbons (including tritium gas) can be measured by using a liquid scintillation counter or a gas proportional counter. (81) (82) Isotopic tracers are not exclusively radioactive.  For instance, $^{13}$C is a non-radioactive element that is suitable for a nonradioactive labeling technique.

       Sensitive analytic procedures enable detection and measurement of very low tracer levels.  In tracer studies, an identifiable tracer material is injected through one or more injection wells into the reservoir being studied.  Water or other fluid is then injected to push the tracer to one or more recovery wells in the reservoir.  The output of the recovery wells is monitored to determine tracer breakthrough and flow through the recovery wells.  Analysis of the breakthrough times and the flows yields important information regarding how to perform the secondary or enhanced recovery processes.

(80) C.Burcham, R.E.Fast, A.S.Murer, and P.S.Northrop. Oil recovery by enhanced
    imbibition in low permeability reservoirs. Patent: US5411086, 1995.
(81) J.S.Tang and B.C.Harker. Use of tracers to monitor in situ miscibility of solvent
    in oil reservoirs during EOR. Patent: US 5111882, 1992.
(82) J.S.Tang and B.C.Harker. Use of tracers to monitor in situ miscibility of solvent
    in oil reservoirs during EOR. Patent: CA 1310140, 1992.

A sharp breakthrough of tracers in a two-well tracer test is achieved by the following method(83):

1. Injecting a solution consisting of a water-soluble tracer and a partitioning tracer that distributes between the formation oil and water into the formation through a temporary injection well.
2. Discontinuing injection into the temporary injection well after a slug of the tracer solution has been injected.
3. Producing formation fluids from the production well
4. Monitoring the concentration of each tracer and the volumes of fluids produced from the producing well borehole
5. Determining the formation of residual oil saturation from the chromatographic separation of the water-soluble tracer and the partitionable tracer

In most production reservoirs, the produced brines are injected into the formation for purposes of maintaining reservoir pressure and avoiding subsidence and environmental pollution. In the case of geothermal fields, the brines are also injected to recharge the formation. However, the injected brines can adversely affect the fluids produced from the reservoir. For example, in geothermal fields, the injected brine can lower the temperature of the produced fluids by mixing with the hotter formation fluids. In order to mitigate this problem, the subsurface paths of the injected fluids must be known.

Tracers have been used to label fluids in order to track fluid movement and monitor chemical changes of the injected fluid. Radioactive materials are one class of commonly used tracers. These tracers have several drawbacks. One drawback is that they require special handling because of the danger posed to personnel and the environment. Another drawback is the alteration by the radioactive materials of the natural isotope ratio indigenous to the reservoir—thereby interfering with scientific analysis of the reservoir fluid characteristics. In addition, the half life of radioactive tracers tends to be either too long or too short for practical use.

A number of organic compounds are suitable for use as tracers in a process for monitoring the flow of subterranean fluids. The following traces have been proposed: benzene tetracarboxylic acid, methylbenzoic acid, naphtalenesulfonic acid, naphthalenedisulfonic acid, naphthalenetrisulfonic acid, alkyl benzene sulfonic acid, alkyl toluene sulfonic acid, alkyl xylene sulfonic acid, α-olefin sulfonic acid, salts of the foregoing acids, naphthalenediol, aniline, substituted aniline, pyridine, substituted pyridines. (84)

A chemical enhanced oil-recovery technology can be used to remove oily contaminants from soil. Laboratory studies demonstrated that a variety of alkaline-surfactant combinations can be used with a polymer to reduce the residual oil saturation in waterflooding. (85)

(83) G.L.Stegemeier and G.E.Perry. Method utilizing spot tracer injection and production induced transport for measurement of residual oil saturation. Patent: US 5168927, 1992.
(84) R.D.Hutchins and D.L.Saunders. Tracer chemicals for use in monitoring subterranean fluids. Patent: US 5246860, 1993.
(85) M.J.Pitts, K.Wyatt, T.C.Sale, and K.R.Piotek. Utilization of chemical-enhanced oil recovery technology to remove hazardous oily waste from alluvium. In Proceedings Volume, pages 33-44. SPE Oilfield Chem Int Symp (New Orleans, LA, 3/2-3/5)1993

Polyaromatic hydrocarbons absorb strongly to humus and other soil components, rendering these contaminants difficult to remove by thermal, physical, or chemical means, and unavailable for biodegradation. To desorb polyaromatic hydrocarbons from soil, surfactant flooding processes and soil-washing processes or treatments to enhance the biodegradation of polyaromatic hydrocarbons have been considered.

However, surfactant flooding may contaminate groundwater. Soil washing requires excavation and biodegradation of polyaromatic hydrocarbons and is incomplete even with surfactants. Biodegradable surfactants that can form reasonably stable foams in the presence of up to 50% ethanol have been developed. These ethanol-based foams can readily desorb the polyaromatic hydrocarbons from gas plant soils and are moving well through soils at pressures of 1.5 psi/ft or less(86) (87). A partially hydrolyzed copolymer of acrylamide and n-octylacrylamide together with sodium alkyl sulfates has also been described for in situ decontamination by flooding operations. (88)

(86) J.J.Kolbane, II, P.Chowdiah, K.J.Kayser, B.Misra, K.A.Jackowski, V.J.SRivastava, G.N.Sethu, A.D.Nikolov, and D.T.Wasan. In-situ remediation of contaminated soils using foams as carriers for chemicals, nutrients, and other amendments. In *Proceedings Volume*. 9th Inst Gas Technol Gas, Oil, & Environ Biotechnol Int Symp (Colorado Springs, CO, 12/9-12/11), 1996.

(87) J.J.Kolbane, II, P.Chowdiah, K.J.Kayser, B.Misra, .A.Jackowski,V.J.SRivastava, G.N.Sethu, A.D.Nikolov, and D.T.Wasan. In-situ remediation of contaminated soils using foams. In *Proceedings Volume*. 10th Inst Gas Technol Gas, Oil, & Environ Biotechnol & Site Remediation Technol Int Symp (Orlando, FL,12/8-12/10), 1997.

(88) R.Varadaraj. Polymer-surfactant fluids for decontamination of earth formations. Patent: US 5614474, 1997.

**Spill Remediation**

The most spectacular incidents concerning oil spills occur in coastal regions. Therefore, most of this section will address this scenario; however, there will be supplemental information concerning subsurface and soil remediation.

Chemical dispersants can be used to reduce the interfacial tension of floating oil slicks so that the oils disperse more rapidly into the water column and thus pose less of a threat to shorelines, birds, and marine mammals. The action of oil spill-treating agents can be divided into four classes: solidifiers, demulsifying agents, surface-washing agents, and dispersants. The majority of oil spill—treating agents, however, are described as dispersants.

Oil spill-treating agents are referred to as:

Oil spill-treating agents
Spill-treating agents
Chemical shoreline cleaning agents (SCAs)
Shoreline cleaning agents
Chemical beach cleaners
Oil spill dispersants
Oil spill cleanup agents

Oil spill-treating agents have been a subject of controversy since their introduction during the Torrey Canyon oil spill off the coast of the United Kingdom in 1967. The dispersant policies of several European nations and Canada have been reviewed and compared with those of the United States. (89)

There are some requirements that oil spill-treating agents should fulfill. Chemical dispersants are often used to disperse spilled oils, which threaten to pollute shoreline areas. Oil spill dispersants increase the surface area of the oil, which accelerates the process of biodegradation. However, the toxic properties of dispersants limit their use.

In particular, oil spill-treating agents should have a long shelf life and should be:

Ecologically friendly
Nontoxic
Nonpolluting
Biodegradable
Highly active
Noncorrosive
Applicable from boats, aircraft, and helicopters

Special formulations that are suitable for various environments, that is, marine, shoreline, freshwater and saltwater, tropic, and artic environments, have been developed.

Mechanisms

Crude oils contain various amounts of indigenous surface-active agents that stabilize water-in-oil emulsions. Therefore crude oils may stabilize such emulsions.

(89) J.M.Cunningham, K.A.Sahatjian, C.Meyers, G.Yoshioka, and J.M.Jordan. Use of dispersants in the United States: Perception or reality? In Proceedings Volume, pages 389-393. 12th Bien API et al Oil Spill (Prev, Behav, Contr, Cleanup) Int Conf (San Diego, CA, ¾-3/7), 1991.

It has been shown that the effectiveness of a dispersant is dependent on both the dispersant type and the specific crude oil(90). However, there is no apparent correlation between the degree of emulsion-forming tendency of the crude oil, which is a function of the indigenous surfactant content, and the effectiveness of the dispersant. In general, indigenous surfactants in crude oil reduce the effectiveness of the dispersant, but to an unpredictable level.

Dispersants are widely used in many parts of the world to deal with oil spills on the ocean. The objective of adding the dispersant is to emulsify the oil slick into the water column. This prevents wind forces form moving the slick to shore and may increase the bioavailability of the oil because of the large increase in surface area caused by emulsification. Dispersants are surface-active agents whose behavior can be understood through application of surface chemical principles. (91)

Modern oil spill-dispersant formulations are concentrated blends of surface-active agents (surfactants) in a solvent carrier system. Surfactants are effective for lowering the interfacial tension of the oil slick and promoting and stabilizing oil-in-water dispersions. The solvent system has two key functions: (1) to reduce the viscosity of the surfactant blend to allow efficient dispersant application and (2) to promote mixing and diffusion of the surfactant blend into the oil film. (92)

A method for treating an oil film floating on water is composed of two functions:
1. Dispersing a number of water-floatable particles on an oil film, the particles of a material that, under illumination and in the presence of air, accelerates the oxidation of organic compounds in the oil film
2. Allowing the particles to be exposed to solar illumination and ambient air (93)

The particles consist of a bead with an exterior surface that is at least partially coated with a material capable of accelerating the oxidation of organic compounds floating on water, under illumination, and in the presence of air. The coated bead is water-floatable and has a diameter of less than 2 mm. The bead consists of a plastic material coated with an intermediate layer of a material that will not accelerate the oxidation of the plastic material by air or by itself, oxidized under illumination and in the presence of air by the outer coating material.

The rise in environmental concern, coupled with the enormity of some oil spills in the recent past, has led to the development of new generations of oil spill dispersants.

Biodegradable oil spill dispersants with high efficiency and low toxicity have been prepared and tested. They consist of nonionic and low-toxicity surfactants with different molecular weights.

(90) G.P.Canevari. Basic study reveals how different crude oils influence dispersant performance. In *Proceedings Volume*, pages 293-296. 10th Bien API et al Oil Spill (Prev, Behav, Contr, Cleanup) Conf (Baltimore, MD, 4/6-4/9), 1987.
(91) C.A.Christopher. Surface chemical aspects of oil spill dispersant behavior. In *Proceedings Volume*, pages 375-389. 4th Annu Pennwell Conf & Exhibit Co Petro (Safe 93) Conf (Houston, TX, 1/26-1/28), 1993.
(92) R.J.Fiocco, R.R.Lesard, G.P.Canevari, K.W.Becker, and P.S.Daling. The impact of oil dispersant solvent on performance. In *Proceedings Volume*, pages 299-309. 2nd ASTM Use of Chem in Oil Spill Response Symp (Victoria, Canada, 10/10-10/11), 1994.
(93) A. Heller, and J.R.Brock. Materials and method for photocatalyzing oxidation of organic compounds on water. Patent: AU 657470, 1995.

The relationship between interfacial tension and the efficiency and chemical structure of the prepared oil spill dispersants was also studied.

A test to determine the biodegradation rate of the dispersant and the degradation rate of the dispersant-oil mixture has been proposed. (94) (95) The test method is intended to supplement the toxicity tests and the effectiveness tests, which evaluate the performance of oil spill dispersants.

Ideally, the consideration of dispersant use should take place before an emergency to reach a timely decision. Several states and regional response teams have active programs that address the planning and technical and environmental considerations affecting dispersant use. In several states where the use of dispersants is an emerging issue, there appears to be a willingness to consider their use on a case-by-case basis and a genuine interest in learning more about their effectiveness and toxicity.

A decision concerning the use of a certain dispersant involves several components, including considerations of operational feasibility and regulatory policy and environmental concerns. Several guidelines have been given for the use of oil spill dispersants, among them, ASTM guidelines for use. (96) The guidelines include a variety of environments such as freshwater ponds, lakes, and streams, as well as land. The laboratory tests to measure dispersant effectiveness that are specified in federal regulations are not easy to perform, nor inexpensive, and generate a large quantity of oily waste water.

Initially, it was emphasized that oil spill-treating agents can be divided into four classes: solidifiers, demulsifying agents, surface-washing agents, and dispersants.

Solidifiers, or gelling agents, solidify oil, requiring a large amount of agent to solidify oil—ranging from 16% to more than 200% by weight. Emulsion breakers prevent or reverse the formation of water-in-oil emulsions.

The effectiveness of a dispersant can be defined as the percentage of oil in the water column. Emulsion breakers have been tested for their performance(97). Among the tested products, only one highly effective formulation has been determined. However, the conclusion is not too discouraging. Many products will work but require large amounts of spill-treating agent. Surfactant-containing materials are of two types: surface-washing agents and dispersants. Testing has shown that an agent that is a good dispersant is, conversely, a poor surface-washing agent, and vice versa. Tests of surface-washing agents show that only a few agents have effectiveness of 25% to 40%, in which this effectiveness is the percentage of heavy oil removed from a test surface. The aquatic toxicity of these agents is an important factor and has been measured for many products.

(94) T.Abdel-Moghny and H.K.Gharieb. Biodegradable oil spill dispersants with high efficiency and low toxicity. In *Proceedings Volume*, volume 1, pages 184-195. 1st Bahrain Soc Eng et al Environ Issues in the Petrol & Petrochem Ind Spec Conf (Manama, Bahrain, 12/4-12/6), 1995.

(95) M.Mulyono, E.Jasifi, and M.Maloringan. Biodegradation test for oil spill dispersant (OSD) and OSD-oil mixture. In Proceedings Volume, pages 355-363. 5th Asian Counc Petrol Conf (Ascope 93) (Bangkok, Thailand, 11/2-11/6),1993

(96) J.Cunningham, M.Rojo, K.J.Kooyoomjian, and J.M.Jordan. Decision-making on the use of dispersants. The role of the states. In Proceedings Volume, pages 353-356. API et al Oil Spill (Prev, Behav, Contr, Cleanup) 20th Anniv Conf (San Antonio,TX, 2/13-2/16), 1989.

(97) M. Fingas, R.Stoodley, and N. Laroche. Effectiveness testing of spill-treating agents *Oil Chem Pollut*, 7(4):337-348, 1990.

Results using the swirling flask test for dispersant effectiveness have been reported. Heavy oils show effectiveness values of approximately 1%, medium crude oils of approximately 10%, light crude oils of approximately 30%, and very light oils of approximately 90%.

The effectiveness of a number of crude oil dispersants, measured using a variety of evaluation procedures, indicates that temperature effects result form changing viscosity, dispersants are most effective as at salinity of approximately 40 ppt (parts per thousand), and concentration of dispersant is critical to effectiveness. The mixing time has little effect on performance, and a calibration procedure for laboratory dispersant effectiveness must include contact with water in a manner analogous to the extraction procedure; otherwise, effectiveness may be inflated(98). Compensation for the coloration produced by the dispersant alone is important only for some dispersants.

As has been frequently noted in this discussion, oil has the tendency to emulsify with the aqueous phase it is in contact with, during any stage of the extraction and transport process. Consequently, a final section will address demulsifiers and their consistent use.

Demulsifiers

In the production of crude oil, the greatest part of the crude oil occurs as a water-in-oil emulsion. The composition of the continuous phase depends on the water/oil ratio, the natural emulsifier systems contained in the oil, and the origin of the emulsion. The natural emulsifiers contained in crude oils have a complex chemical structure, so that, to overcome their effect, petroleum-emulsion demulsifiers must be selectively developed. As new oil fields are developed, and as the production conditions change at older fields, there is a constant need for demulsifiers tha lead to a rapid separation into water and oil, as well as minimal-residual water and salt mixtures.

The emulsion must be separated by the addition of chemical demulsifiers before the crude oil can be accepted for transportation. The quality criteria for a delivered crude oil are the residual salt content and the water content. for the oil to have a pipeline quality, it is necessary to reduce the water content to less than approximately 1.0%.

The separated saltwater still contains certain amounts of residual oil, where now preferentially oil-in-water emulsions are formed. The separation of the residual oil is necessary in oil field water purification and treatment for ecologic and technical reasons, because the water is used for secondary production by waterflooding, and residual oil volumes in the water would increase the injection pressure.

The presence of water-in-oil emulsions often leads to corrosion and to the growth of microorganisms in the water-wetted parts of the pipelines and storage tanks.

At the refinery, before distillation, the salt content is often further reduced by a second emulsification with freshwater, followed by demulsification. Crude oils with high salt contents could lead to breakdowns and corrosion at the refinery. The object of using an emulsion breaker, or demulsifier, is to break the emulsion at the lowest possible concentration and, with little or no additional consumption of heat, to bring about a complete separation of the water and reduce the salt content to a minimum.

(98) M.F.Fingas, B.Kolokowski, and E.J.Tennyson. Study of oil spill dispersants effectiveness and physical studies. In Proceedings Volume, pages 265-287. 13th Environ Can Artic & Mar Oil Spill Program Tech Semin (Edmonton, Canada, 6/6-6/8), 1990.

There are oil-soluble demulsifiers and water-soluble demulsifiers, the latter being widely used. Emulsions are variable in stability. This variability is largely dependent on oil type and degree of weathering. Emulsions that have a low stability will break easily with chemical emulsion breakers. Broken emulsions will form a foamlike material, called *rag*, which retains water that is not part of the stable emulsions. The most effective demulsifiers must always be determined for the particular emulsion.

Demulsifiers are often added to the emulsion at the wellhead to take advantage of the temperature of the freshly raised emulsion to hasten the demulsification step.

During improved oil-recovery processes, waterflooding of the oil is applied. The entrained water forms a water-in-oil emulsion with the oil. In addition, salts such as sodium chloride, calcium chloride, and magnesium chloride may be dissolved in the emulsified water.

Demulsifiers (specifically, oil spill demulsfiers) can be applied to oil spills in low concentrations. They prevent mousse formation for significant periods of time and cause a large reduction in oil-water interfacial tension. The best of these was found to prevent emulsification at dosages as low as 1 par inhibitor to 20,000 parts of fresh oil at 20°C(99). At dosages of 1:1000, at temperatures higher than 10°C, the chemical also results in significant and rapid dispersion of the oil. For very low temperatures or highly weathered oil, the performance of the chemical falls off sharply.

Desired Properties

Demulsifiers for crude oil emulsions should meet the following properties:

> 1. Rapid breakdown into water and oil with minimal amounts of residual water
> 2. Good shelflife
> 3. Quick preparation

The stabilization of water-oil emulsions happens as a result of the interfacial layers, which mainly consist of colloids present in the crude oil—asphaltenes and resins. By adding demulsifiers, the emulsion breaks up. With water-soluble demulsifiers, the emulsion stabilizers originally in the system will be displaced from the interface. In addition, a change in wetting by the formation of inactive complexes may occur. conversely, using oil-soluble demulsifiers, the mechanism, in addition to the displacement of crude colloids, is based on neutralizing the stabilization effect by additional emulsion breakers and the breakup resulting from interface eruptions. (100)

The effectiveness of a crude oil demulsifier is correlated with the lowering the shear viscosity and the dynamic tension gradient of the oil-water interface. The interfacial tension relaxation occurs faster with an effective demulsifier. Short relaxation times imply that interfacial tension gradients at slow film thinning are suppressed. Electron spin resonance experiments with labeled demulsifiers indicate that the demulsifiers form reverse micellelike clusters in the bulk oil.

(99) L.A.Buist and S.L.Ross. Emulsion inhibitors: A new concept in oil spill treatment. In Proceedings Volume, pages 217-222. 10th Bien API et al Oil Spill (Prev, Behav, Contr, Cleanup) Conf (Baltimore, MD, 4/6-4/9), 1987.
(100)M.Kotsaridou-Nagel and B.Kragert. Demulsifying water-in-oil emulsions through chemical addition (Spaltungsmechanismus von Wasser-in-Erdol-Emulsionen bei Chemikalienzusatz). *Erdon Erdgas Kohle*, 112(2):72-75, February 1996.

The slow unclustering of the demulsifier at the interface appears to be the rate-determining step in the tension relaxation process. (101) (102)

## Demulsifiers

| Demulsifier | Type | Demulsifier | Type |
|---|---|---|---|
| Blends containing (1) tannin or amino methylated tannin, (2) a cationicpolymer(3)polyfunctinal amines | WiO | Polyalkylenepolyamides-amines | Oiw,Wio |
| Copolymer of diallyldimethy ammonium chloride and quaternized amino alkylmethacrylates and (meth)acrylic esters (e.g.,2-ethylhexylacrylate) | OiW | Fatty acid N,N-dialkylamides (c) | OiW |
| Amphoteric acrylic acid copolymer | OiW | Diamides from fatty amines (d) | WiO |
| Branched polyoxyalkylene copolyesters | OiW | Polycondensates of oxalkylated fatty amine (d) | OiW |
| Copolymer of esters of acrylic acid and the respective acids, methacrylic acid (a) | WiO | Poly(diallyldimethyl ammonium chloride) | OiW |
| Copolymer of polyglycol acrylate or methacrylate esters | OiW | Alkoxylated fatty oil | |
| Poly(1-acryloyl-4-methyl piperazine and copolymers of 1-acryloyl-4-methyl piperazine quaternary salts with acrylamide quaternary salts | OiW | Oxalkylated polyalkylene polyamines | WiO |
| Copolymers of acrylamidopropyltrimethyl ammonium chloride with acrylamide | OiW | Crosslinked oxalkylated polyalkylene polyamines | OiW |
| Vinyl phenol polymers (b) | OiW | Phenol-formaldehyde resins, modified with benzylamine (e) | |
| Etholylated or epoxidized polyalkylene glycol | WiO | Alkoxylated alkylphenol-formaldehyde resins | WiO |
| Polymers from dimethylaminoethyl methacrylate, dimethylaminopropyl methacrylamide | OiW | Phenol-formaldehyde polymer modified with ethylene carbonate | WiO |
| Polymer of monoallylamine | OiW | Modified phenol-formaldehyde resins | |
| Copolymers ofallyl-polyoxyalkylenes with acrylics | WiO | Polyalkylene polyamine salts | OiW |
| Copolymer of diallyldimethyl ammonium chloride and vinyl trimethoxysilane | WiO | Dithiocarbamate of bis-hexamethylenetriamine | OiW |
| Cationic amide-ester compositions | OiW | Di- and tri-dithiocarbamic acid compounds | |
| Polythioalkyloxides | WiO | Sulfonated polystyrenes | OiW |
| Polyether-polyurethanes | WiO | Asphaltenes | |
| Polyurea-modified polyethrurethanes | WiO | Acid-modified polyol | LS |

LS, liquid-solid separation; OiW, oil-in-water use; WiO, water-in-oil use

(a) Up to five comonomers
(b) Hydrolysis of polyacetoxystyerene
(c) Sludge or emulsion during the drilling or workover
(d) Act also as corrosion inhibitors
(e) Demulsifying at 65° - 70°C

(101) D.Tambe, J.Paulis, and M.M.Sharma. Factors controlling the stability of colloid-stabilized emulsions. Pt 4:Evaluating the effectiveness of demulsifiers. *J Colloid Interface Sci*, 171(2):463-469, May 1995.
(102) S.Mukherjee and A.P. Kushnick. Effect of demulsifiers on interfacial properties governing crude oil demulsification. In Proceedings Volume. Annu AICHE Mtg (New York, 11/15-11/20), 1987.

**Chapter 6: Conclusion**

Recommendations:

Oilfield process chemicals are the chemicals used to support the exploration and processing of oil and natural gas in the field. Various factors have contributed to the fluctuations in demand for oilfield process chemicals. Presently, the U.S. and other countries use more oil than they are capable of producing. This generates an increase in exploration and production both domestically and internationally in order to compensate increased U.S. and worldwide demands. The additional exploration, the development of new oil and natural gas wells, and the increased production in existing oil and gas wells results in an increase in the demand and sale of oilfield process chemicals.

This thesis was composed to evaluate the future of the oilfield process chemicals industry on a worldwide scale. The forecasted demand and production of oil will have a direct impact on the demand for oilfield process chemicals. Current estimates state that the five-year forecast for the oilfield process chemicals industry from 2002 through 2007 will grow exponentially. This volatile industry has recently experienced an increase in sales resulting from new oil discoveries, political drivers and advances in technology. Based upon this information, many industry "thinktanks" forecast the oilfield process chemicals industry will grow at an average annual growth rate (AAGR) of 6.6% over the next five years. This estimation is based upon projections in the oil drilling, exploration, and production sectors.

The following pages detail some operational parameters for research, reservoir evaluation, drilling, production, and transport that should optimize the use of chemical remediation. (103)

- Use an integrated process which includes a multi-disciplinary team including service companies.
- Select a few wells for establishing the credibility of the process. Try a few wells with a greater chance of success. Then, select the more difficult ones.
- Train the field personnel and supervise operations so that minute details are not overlooked.
- May need to shut in producers in some cases to allow water injection to catch up.
- Re-injecting produced water can be the most economic and environmentally friendly option.
- Use the geo-engineering model to look at various development scenarios and keep simulation "live" for reservoir management.
- Use fully integrated multidisciplinary teams representing all assets to develop a broader water management plan. The Asset Team cannot do it alone!
- Utilize a complete diagnostics approach to achieve success.
- Work on a collaborative basis with other operators and service companies to develop and implement new technology.
- Distributed temperature measurement is an improved method of obtaining injection profiles. Fiber optics is a good means of collecting these data.
- Use of smart wells along with the distributed temperature sensor.
- Use of biological filters for produced water cleaning.

(103) http://www.spe.org/spe/jsp/basic/0,,1104_1575_1040464,00.html

- Waterflooding should be part of the initial development plans, especially offshore.
- When addressing water control in producing wells, it is important to identify the type of water entry mechanism and other diagnostics, prior to selecting an appropriate solution.
- Chances of water shut-off job success can be improved when the number of candidate wells evaluated is widened and then narrowed down systematically to a few ranked ones.  It may not be as prudent to first address the wells with significant problems as it would be to choose those that are diagnosed to offer better chances of success.
- Artificial lift should be considered early in the development planning.
- Injecting above fracturing pressure and below fracturing pressure are both applicable under the right conditions. Since there are ample data (from North Sea) to support the presence of waterflood induced fractures, it is worthwhile to mention that intentional fracturing may be considered as part of the field development planning as this may enable a significant cost savings in term of reduction in the number of injection wells, and well stimulation and offshore facilities costs. The concept of matrix vs fracture injection was discussed in both the general and breakout sessions.
- Multiple fracs result in shorter frac lengths.
- Since it is difficult to understand and model how fractures grow, it is important to have a sound monitoring program.
- To gain confidence, it is advisable to use proven technology for given well conditions.
- Evaluate the entire field asset, not just a single well for success or failure. Also, execute the plan from start to finish.
- On-site WSO (water shut off) job/operation supervision is critical for success. Therefore, we should pay attention to minute details of operations.
- We must know the downhole mechanical configuration before starting a workover operation.
- Temperature at the wellhead is indicative of the flowing fluids, but it is difficult to see breakthrough from wellhead temperature.
- Knowing water entry point is critical.
- Fiber optics can be used outside casing. However, perforating techniques will have to be developed.
- The fiber optics technique requires some judgment, but compared to PLTs, it is significantly easier to use, especially in horizontal wells.
- We should take time to train operation personnel in managing water quality.
- Water quality out of specification can have a huge impact on oil production due to inability to inject.
- It is important to add nitrate to sea water before injection to reduce corrosion due to Sulfate Reducing Bacteria (SRB).
- Sometimes, it is advisable not to pull packers, but to do side-tracks instead as they may be more cost effective.
- Fine mobilization can play a key role in permeability reductions.
- Compact separation: In many cases, there is no need for large facilities. Select technology usage appropriately. (103)

(103) http://www.spe.org/spe/jsp/basic/0,,1104_1575_1040464,00.html

General Discussion:

 The oilfield industry has changed dramatically over the past century. Technologically, the demands for efficient extraction in a timely manner have yielded a genre of engineering changes that are optimizing the process. The reach of this industry is expanding to the harshest of environments on or below the surface of the earth. As a consequence or more correctly, as the thirst for more hydrocarbons increases, the science of drilling, producing, and transporting will foster the corporate mentality of cost/benefit ratio analysis on a global scale.

 The act of removing a nonrenewable resource from a subsurface formation has to be recognized as an invasive procedure that will have inevitable consequences. Slowly, the realization of the long-term effects of such an action, are now being published. When an entity engages in hydrocarbon extraction, they are coming in contact with a dynamic environment that is not static but the result of a state of equilibrium that has taken untold years to reach. Any action taken to remove such causes consequential changes. Any chemical applications or remediation measures may either reduce or exacerbate the problem. This is where research and cooperation between all parties involved helps to mitigate such problems both now and for future needs.

 Currently, there has been a move to utilize chemical compounds that promote synergy. Application of basic chemical science and reactive tendencies has aided in the production of such assets. Amazingly, the move to formulate these may also herald a new direction for energy management and development of new energy sources.

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(9) http://www.glossary.oilfield.slb.com/Display.cfm?Term=mud

(8)  http://www.glossary.oilfield.slb.com/Display.cfm?Term=viscosity

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**Appendix:**

**Chart M-1**

- **The projected annual growth of the oilfield chemicals market is 6.6% per year between 2002 and 2007.**

- **The market should reach a value of $2.3 billion annually by 2007.**

- **Enhanced oil recovery (EOR) applications will increase by an average annual growth rate (AAGR) of 22% between 2002 and 2007.**

- **The peak demand for oil will occur around 2015, delaying the decline in production until 2016.**

**Value of Oilfield Process Chemicals by Application, 2002 and 2007 ($ Millions)**
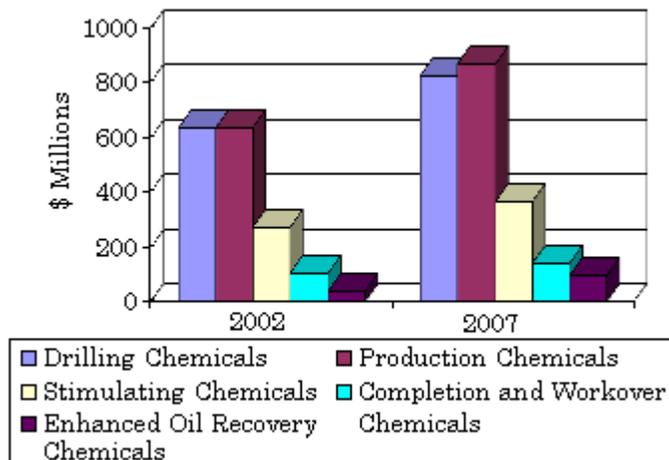


**Source: BCC, Inc.**

**Image M-1**
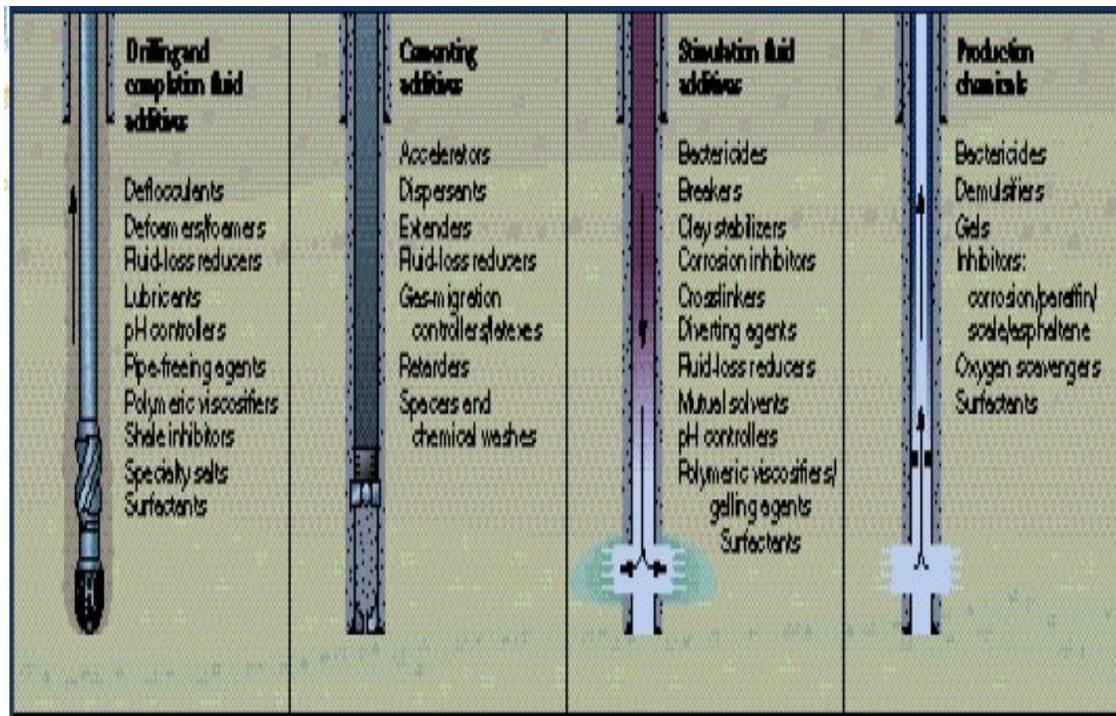


Categories of specialty oilfield chemicals used at the wellsite. Hundreds of different chemical compounds are pumped downhole during the lifetime of a typical oil or gas well. Specialty additives provide the necessary fluid properties required for basic drilling, cementing, completion, stimulation and production operations at bottomhole temperatures and pressures. Although the most important additives vary from well to well, those listed here represent a typical set.

(Courtesy Oilfield Review Magazine, Spring 1997, pg. 27)

**Image M-2**

Environmental actions impacting the application of oilfield chemicals. The USA has been the leader in enacting legislation protecting the environment, with many of the major milestones shown on the time line. Several regulations have directly or indirectly influenced the use of specialty oilfield chemicals. As the United Nations (UN) and other organizations representing countries around the world became involved, the impact broadened, as shown by milestones designated with an asterisk(*).

From 1880 to 1960, the US Congress passed a total of eight acts related to the environment. Six more followed from 1960 to 1969. From 1970 to 1990, however, the trend accelerated dramatically, and 50 acts were passed—ranging from the creation of the Environmental Protection Agency (EPA) to establishment and amendment of the Superfund Act. In addition, international actions by OSPARCOM—the Oslo and Paris Commissions for the Protection of the Marine Environment of the

Northeast Atlantic—set the foundation for laws governing protection of oceans and coastlines from hydrocarbons, and regulations for disposal of offshore platforms.

US laws intended to preserve unexploited natural wilderness and wetlands areas have reduced or prevented seismic activity in certain areas and prompted the development of sophisticated seismic and wireline tools and software to limit environmental impact. Air and water emission and waste restrictions have led to

| 1963 | 1964 | 1965 | 1968 | 1970 | 1972 | 1972 |
|---|---|---|---|---|---|---|
| Clean Air Act | Wilderness Act | Water Quality Act  Solid Waste Disposal Act | Wild and Scenic Rivers Act  National Trail System Act | National Environmental Policy Act  OSHA and EPA created | Oslo Commission*  UN Plan for Protection of the World Environment*  Clean Water Act  Coastal Zone | Paris Commission*  Safe Drinking Water Act |

improved techniques to decrease or eliminate unwanted off-gas and water production. Disposal considerations have changed the nature of oilfield chemical packaging from small, disposable containers to large, reusable containers. Radiation laws have spurred development of surface and downhole tools that rely on nonradioactive instead of radioactive sources.

In the US, the dominant laws affecting the oil field have been RCRA and CERCLA/Superfund. Although passed in 1976

and 1980, respectively, it took several years for the agencies involved to promulgate enforceable regulations. Oil and gas E&P activities were exempt from these regulations during the industry's restructuring period in the mid- to late-1980s. In return, 9.7 cents of each barrel of produced or imported oil went to Superfund.

In the North Sea, actions by OSPARCOM have impacted exploration, drilling, cementing and stimulation practices. Drilling fluids have moved from oil-base

to synthetic or water-base systems. Stimulation treatments now include corrosion inhibitors, crosslinkers and other additives with lower toxicity.

On a global basis, developing nations are facing similar environmental issues. Chile, for example, is expected to issue enforceable environmental regulations later this year. Many countries are considering requiring ISO 14000 or a similar standard as a management system to foster proactive, beyond-compliance environmental activities.

| 1976 | 1977 | 1980 | 1986 | 1991 | 1996 |
|---|---|---|---|---|---|
| Resource Conservation and Recovery Act —RCRA | Toxic Substance Control Act—TSCA | Comprehensive Environmental Response, Compensation and Liability Act —CERCLA/Superfund | Superfund Amendment Reauthorization Act—SARA | Wetlands Executive Order | ISO 14000/14001 Standards for Environmental Management* |

(Courtesy Oilfield Review Magazine, Spring 1997, pg. 28-29)

**Chart M-2**

## Classification of Drilling Muds

| Class | Description |
|---|---|
| Freshwater muds—dispersed systems | pH from 7 – 9.5, include spud muds, bentonite-containing muds, phosphate-containing muds, organic thinned muds(red muds, lignite muds, lignosulfonate muds), organic colloid muds |
| Inhibited muds—dispersed systems | Water-based drilling muds that repress hydration of clays (lime muds, gypsum muds, seawater muds, saturated saltwater muds) |
| Low-solids muds—nondispersed systems | Contain less than 3% - 6% v-v solids Most contain organic polymer |
| Emulsions | Oil in water and water in oil (reversed phase, with more than 5% water) |
| Oil-based muds | Contain less than 5% water; mixture of diesel fuel and asphalt |

## Classification of Bentonite Fluid Systems

| Solid-solid interactions | Inhibition level | Drilling fluid type |
|---|---|---|
| Dispersed | Noninhibited | Freshwater clay NaCl<1% $Ca_{+2}$<120 ppm |
| Dispersed | Inhibited | Saline fluids Na+, Ca2+(seawater salt, saturated salt, gypsum, lime) |
| Nondispersed | Noninhibited | Freshwater low solids |
| Nondispersed | Inhibited | Salt and polymer fluids |

**Chart M-3**

WATER CAN LEAVE THE GEL AND LEAK OFF THROUGH THE FRACTURE
FACES, BUT CROSSLINKED POLYMER CANNOT.

Before gelation, fluid gelant solutions can readily leakoff from fractures into porous rock.
However, after gelation, the crosslinked materials will not penetrate significantly into the
porous rock. Thus, formed gels must extrude through fractures during the placement
process. In other words, the crosslinked polymer moves through the fracture as a semi-
solid and does not penetrate past the fracture faces into the porous rock. .
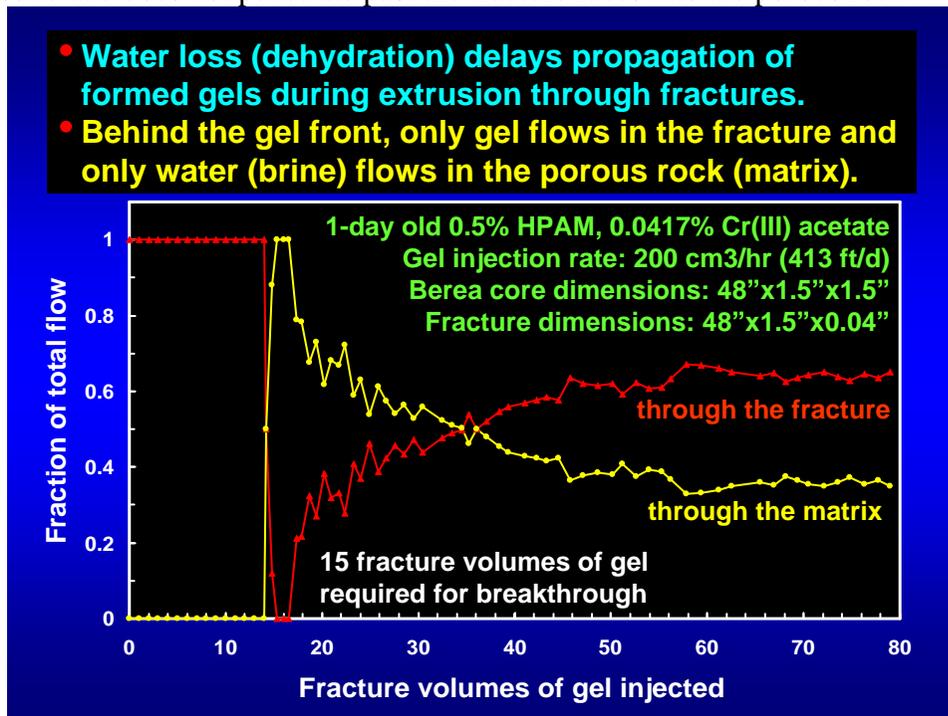


Figure 1—Gel dehydration delays gel propagation through fractures.

http://baervan.nmt.edu/randy/filter_cake/H/