CHAPTER 43
OIL FIELD WATER TECHNOLOGY

THEORY OF OIL FORMATION

The organic theory, the most generally accepted hypothesis on the origin of oil, presumes that microscopic plant and animal life from the sea and tidal areas provided oil's raw materials, hydrogen and carbon. A less prevalent theory proposes that methane and possibly other related hydrocarbons originate in the earth's mantle and work their way to faults and traps in the crust. This theory has gained support because of fairly recent findings of hydrocarbons in meteorites and in the more distant planets.

According to the prevailing theory of the biological origin of oil and gas, through millions of years, rivers transported great volumes of mud, sand, and products of surface erosion to the sea floor, to be spread by tides and currents. Under the increasing weight of this accumulating debris, the ocean floors slowly sank and were compressed to form the sedimentary rocks which contain petroleum—sandstone, shale, porous limestone, and dolomite, a mixture of calcium and magnesium carbonates.

The organic components of trapped microscopic organisms were changed over millions of years to petroleum, through chemical, physical and biological influences (Figure 43.1).

Naturally occurring petroleum is complex and variable in chemical composition. Its color ranges from light greenish brown to black. It may be fluid or so viscous as to be nearly solid. The petroleum refiners classify crudes according to their base as follows:

1. Paraffin-base: High in wax and lube oil fractions, containing small amounts of naphthenes or asphalt; low in sulfur, nitrogen, and oxygen compounds.


4. Aromatic-base: High in low molecular weight aromatic compounds and naphthene, with smaller portions of asphalt and lube oils.

Crudes are commonly identified by API gravity, a figure which is inversely related to specific gravity (sp. gr.).

\[
\text{API gravity} = \frac{141.5}{\text{S.G.}} - 131.5^\circ
\]

43.1
API gravity can be confusing to those unfamiliar with petroleum terminology. In the oil industry, a "high-gravity crude" is rich in volatile materials and has a low specific gravity (0.75 to 0.84), so the API gravity is in the range 35 to 55°. Some "heavy crudes" have a specific gravity close to that of water, and the API gravity may be as low as 15° at the standard temperature of 60°F (16°C).

**THE OIL-BEARING RESERVOIR**

Petroleum, found only in porous sedimentary rock, migrates laterally and upward reaching some local structure or trap having a caprock seal which contains the oil, creating the reservoir.
Many different shapes, sizes, and types of geologic structures form reservoirs. These include: (1) domes and anticlines, (2) fault traps, (3) unconformities, (4) dome and plug traps, (5) lens-type traps, and (6) combination traps. An anticlinal type of folded structure is shown in Figure 43.2, and a trap resulting from faulting is shown in Figure 43.3.

The length and width of a reservoir can vary from one to several miles, and the depth from a few feet to several hundred. A 1 acre (0.405 ha) reservoir with a depth of 10 ft (3.05 m) would contain 10 acre-ft, a common unit of measure. To estimate its petroleum content, the total pore volume (porosity) and percentage oil saturation (10 to 99%) must also be known. The remaining fluid is interstitial (or connate) water. The U.S. standard of measurement of volume in the petroleum industry is the barrel (42 gal, 5.62 ft$^3$, 0.16 m$^3$).

A 10 acre-ft reservoir contains 435,600 ft$^3$ (12,327 m$^3$). With a porosity of 20% and an oil saturation of 80% this would contain:

\[ 435,600 \times 0.2 \times 0.8 = 69,696 \text{ ft}^3 \text{ of oil (1972 m}^3\text{) } \]

\[ = 12,424 \text{ barrels} \]

**PETROLEUM PRODUCTION**

When the drill penetrates the reservoir, oil and gas are forced to the surface by natural reservoir pressure. The period of time during which oil is produced by natural reservoir pressure is referred to as primary production, a period of a few months or several years.

The flowing well is constructed of "strings" of concentric vertical pipes called casings and a smaller pipe, usually 2 to 3 in (5 to 7.5 cm) in diameter, called
FIG. 43.4 The typical arrangement of casing, string, and tubing in an oil well. (Courtesy of American Petroleum Institute, from "Primer of Oil and Gas Production.")

FIG. 43.5 This large "Christmas tree" is made up of 4-in valves and fittings designed for 10,000 lb/in² working pressure. (Courtesy of McEvoy Oilfield Equipment Company.)
tubing, through which produced fluid flows. The largest diameter casing (the surface string) extends to a depth of 200 to 1500 feet (61 to 460 m); the intermediate string may reach a depth of up to 5000 feet (1530 m); a third casing (the oil string) may reach the producing zone. Some producing zones are at depths of 20,000 feet (6100 m) or more. The tubing into the producing formation is secured by a packer which seals the space between the tubing and the final casing (Figure 43.4). Occasionally intermediate level strings are perforated, allowing production to flow simultaneously from shallower producing zones.

A series of valves and flanges at the wellhead (called a "Christmas tree") includes a small orifice plate (called a "choke") (Figure 43.5) to control flow. When the natural reservoir energy subsides, some method of pumping is employed to maintain production (Figure 43.6).

**Oil Dehydration**

Oil leaving the producing well is a mixture of liquid petroleum, natural gas, and formation water (Figure 43.7). During early primary production, water may be insignificant. Most production, however, contains sizable proportions of produced water (up to 90%). This must be separated from the oil since pipeline specifications stipulate maximum water content—as low as 1%, but up to 3 to 4% in some localities.

The initial separation vessel in a modern treating plant is called a free-water-knockout (FWKO) (Figure 43.8). Free water, defined as that which separates within 5 min, is drawn off to a holding tank, to be clarified prior to reinjection or discharge. The remaining oil usually contains emulsified water and must be further processed to break the emulsion, usually assisted by heat, electric energy, or both.

Heater treaters (Figure 43.9) are vertical or horizontal vessels in which the water-in-oil emulsion is resolved, invariably with the assistance of emulsion-
FIG. 43.7 Oil is almost always produced as an emulsion, very different in appearance from finished oil products.

FIG. 43.8 Free water and gas are separated from the produced fluid in this gravity separation vessel, simplifying emulsion breaking. (Courtesy of American Petroleum Institute from "Treating Oil Field Emulsions.")

FIG. 43.9 This heater-treater uses the heat of combustion of gas or oil to heat the emulsion from the free water knockout drum, assisting chemical treatment to yield an oil of minimum water content. (Courtesy of American Petroleum Institute, from "Treating Oil Field Emulsions.")
breaking chemicals. The electrostatic treater employs heat, but also uses high-voltage alternating current to charge the water droplets, accelerating the process of coalescing smaller droplets into larger drops. The demulsified crude oil flows to a stock tank for pipeline shipment to a refinery.

**Enhanced Recovery**

Enhanced recovery describes any additional production after primary production that results from the introduction of artificial energy into the reservoir. This includes waterflooding, gas injection, and other processing involving fluid or energy injection whether for secondary or tertiary oil recovery.

Secondary recovery is any enhanced recovery first undertaken in the reservoir. Usually, it follows primary production, but may be conducted concurrently with it. Waterflooding is the most common method of secondary recovery.

Tertiary recovery is enhanced recovery undertaken following secondary operations designed for total recovery of the remaining petroleum. As much as 50% of the original oil may remain in place after primary and secondary processes are terminated.

**Secondary Recovery by Waterflooding**

Waterflooding is injection of water as a uniform barrier through the producing formation from a series of injection wells toward the producing well. Such injection wells can either be converted producing wells or new wells drilled specifically for injection of a flooding water.

Proper spacing of the injection wells is important. Most reservoirs are flooded through wells distributed uniformly throughout the reservoir. Others may be flooded by peripheral injectors.

A typical arrangement, called a “five-spot pattern,” is shown in Figure 43.10. The density of well spacing (the area enclosed by the perimeter of the five-spot pattern) may be 3-acre, 5-acre, or whatever density is determined to be most efficient by the reservoir engineer.

The permeability of the reservoir rock has a great bearing on its suitability for waterflooding. Rock is considered permeable if a significant fluid flow will pass through it in a short time; it is impermeable if the rate of passage is negligible.

The unit of permeability is the darcy, standardized by the American Petroleum Institute as follows: “A porous medium has a permeability of one darcy when a single phase fluid of one centipoise viscosity that completely fills the voids (or pores) of the medium will flow through it at a rate of one centimeter per second per square centimeter of cross-sectional area under a pressure or equivalent hydraulic gradient of one atmosphere (760 mm of Hg) per centimeter.”
The permeabilities of formation cores are generally in the range of 5 to 1000 millidarcies (md) (1 md = 0.001 d). A rough practical example of 1d would be 1 ft³ (0.0283 m³) of sandstone passing approximately one barrel of oil (0.16 m³) per day with a pressure drop of 1 lb/in² (0.068 bars, 0.0703 kg/cm²).

Permeability and porosity vary greatly both laterally and vertically in the typical reservoir rock. A rock whose permeability is 5 md or less is called a "tight sand" or a "dense limestone" according to its composition. The following are rough permeability ratings:

- 1 to 10 md Fair permeability
- 10 to 100 md Good permeability
- 100 to 1000 md Very good permeability

It is imperative for efficient flooding that the water be totally compatible with the reservoir formation. A desirable water for this purpose is that produced from

![Diagram of field test unit for evaluating permeability and plugging tendency of a core subjected to a specific flood water.](FIG. 43.11)
the formation, after separation from the oil and gas. However, the amount of water required for flooding far exceeds the volume produced, so supplemental water is needed.

Produced water and supplemental surface waters must be clarified to remove residual oil accumulations, sand, or dirt washed from the producing formation, oxidized inorganic or organic suspended solids, or corrosion products. Quality required for waterflooding is dictated by the permeability restriction of the reservoir. Currently, the most popular equipment for clarification is the flotation cell employing gas diffusion to produce clear effluent.

Where injection water must include surface or well water of lower salinity than the original formation water, chemical incompatibility with the formation rock may result. This may cause swelling of clay in the reservoir rock. Historically, the suitability of injection water has been determined through analyses of the waters in question, a membrane filtration, or laboratory work with formation cores. All of these procedures have the disadvantage that the waters have been removed from the actual reservoir environment and may have changed.

A field unit has been developed for defining injection water quality standards (Figure 43.11). The injection water does not undergo any change during sampling, handling or shipment, and storage. Formation rock is used in the study of the effect of chemical additions and filtration conditions.

FIG. 43.12 In this waterflooding operation, both sand filters and septum-type filters are used to prevent underground plugging. (Courtesy L*A Water Conditioning Company.)

Most injection waters are passed through some type of filter, the media and design depending on the reservoir permeability. Types of filters include mixed media beds, individual well cartridges, or septum filters using diatomaceous earth as a filter aid (Figure 43.12). In some cases more sophisticated treatment, such as clarification or lime softening, may be needed. Deaeration may be required to reduce corrosion or to prevent iron oxidation (Figure 43.13).
SECONDARY RECOVERY BY STEAM FLOODING

Water flooding is not effective for secondary recovery of low API-gravity oil from relatively shallow formations at temperatures below about 120°F. This situation responds, however, to steam flooding. Sometimes the steam is used to stimulate an oil well: The well is taken out of service and steam is injected for a period of several weeks to heat the oil-bearing rock; then the oil well is returned to service until stimulation may be required again. (This is known as the "huff-and-puff" method of steaming). The most common method of steaming, however, is introduction of the steam-water mixture from a once-through steam generator into one of a group of centrally located displacement wells, with the steam and hot water then radiating outward toward the peripheral oil wells served by each of the injection wells.

In the Imperial Valley of central California, crude oil having an API gravity of about 11 to 13, and occurring in a very loose formation at depths of 500 to 1500 ft, is recovered by the displacement method of steam injection. In the United States, this area is the largest producer of oil by steaming; the total California
production by this process is about 375,000 bpd. About 30% of the crude produced is used as fuel in the steam generators, although some generators are gas-fired, either continuously or intermittently, as may be required to meet air emission standards.

As time passes at any steam-flood site, there is a gradual increase in temperature of the produced fluids to about 160 to 180°F (71 to 82°C). The wells produce 6 to 8 bbl of water per barrel of oil. The oil and water are separated in dehydration tanks using emulsion breakers, and the water must then be processed to render it suitable for feed to the steam generators and for disposal. The salinity and chemical characteristics of the produced water vary greatly from one site to another. Table 43.1 includes the analysis of several produced waters after the dehydration tanks. Even though these waters are softened, chemically deaerated, and chelated, it is still surprising that such high-salinity waters could be suitable feed water for steam generators that sometimes operate at pressures over 1000 lb/in².

Figure 43.14 shows a typical flow diagram of a water treatment plant servicing a steam-flooding facility. After dehydration, oil is removed in dispersed-air flotation units (see Chapter 9), assisted by cationic emulsion breakers. The skimnings are recovered and treated water is discharged to storage. The flotation unit and storage tanks are gas blanketed to avoid pickup of oxygen. An oxygen scavenger is usually applied at this point. If the Stiff-Davis index is strongly scaling, a stabilizing inhibitor is also applied here to prevent problems owing to calcium carbonate scale. Gypsum (calcium sulfate) may also be a problem. The water is then polished through septum-type filters, Figure 43.12. (See also Figure 11.11.) A variety of filter aids can be used, including specially processed cellulose, diatomaceous earth (DE), and vermiculite. The filter is first precoated by recirculation; then it is put onstream, with a continuous application of filter aid (body feed) of 2 to 3 ppm per ppm oil.

The filtered water is then softened through zeolite softeners (Figure 43.15). The high salinity of the produced water makes softening difficult, so almost universally, a polishing softener follows the primary unit to assure zero hardness in the finished water. The softened water is then sent to the various steam generators in different areas of the oil field—sometimes several miles away.

The steam generator is unusual in that it is a once-through unit (Figure 43.16). Feed water is preheated (to avoid acid deposit attack of the economizer), and then flows through the economizer to recover heat from the stack gas. The feed water then passes through the radiant and convection sections of the steam generator where steam is generated. However, unlike conventional drum-type boilers, the fluid leaving the generator has a quality of 80%; that is, it contains 80% steam and 20% water by weight. Because the steam volume at 900 lb/in² is 0.49 ft³/lb, where the specific volume of water is only 0.021 ft³/lb, the discharged fluid contains 99% steam by volume and only 1% water by volume.

However, the water in the discharged steam contains all of the solids contained in the feed water. At 80% quality, 5 lb of feed water produces 4 lb of steam and 1 lb of water, so the solids have been concentrated 5 times. The relationship between steam quality and concentration is:

\[
CR \text{ (concentration ratio)} = \frac{100}{100\text{-quality}}
\]

Depending on the depth of the injection well and the permeability of the formation, the steam generators may operate at a pressure as low as 300 lb/in² and as high as 1000 (68 bars). This pressure is maintained by the boiler feed pumps.
**Table 43.1** Analyses of Several Formation Waters

<table>
<thead>
<tr>
<th>State</th>
<th>County</th>
<th>Formation</th>
<th>Constituents, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Na</td>
</tr>
<tr>
<td>Oklahoma</td>
<td>Kingfisher</td>
<td>Oswego</td>
<td>56,250</td>
</tr>
<tr>
<td>Kansas</td>
<td>Ellis</td>
<td>Arbuckle</td>
<td>16,800</td>
</tr>
<tr>
<td>New Mexico</td>
<td>Lea</td>
<td>San Andreas</td>
<td>9,150</td>
</tr>
<tr>
<td>Texas</td>
<td>Hopkins</td>
<td>Paluxy</td>
<td>5,640</td>
</tr>
<tr>
<td>California</td>
<td>Kern†</td>
<td></td>
<td>3,936</td>
</tr>
<tr>
<td>California</td>
<td>Kern</td>
<td></td>
<td>6,725</td>
</tr>
<tr>
<td>California</td>
<td>Kern (Kern River)</td>
<td></td>
<td>184</td>
</tr>
</tbody>
</table>

* The form for water analysis reporting recommended by the American Petroleum Institute is shown in Figure 43.14.
+ These brines are treated and used as feed water to 800 to 1000 lb/in² steam generators in steam flooding applications.
FIG. 43.14 Treatment of produced water for steam flooding.

FIG. 43.15 Two-stage sodium zeolite softening of deoiled, filtered, produced water to render water suitable for high-pressure boiler.
FIG. 43.16 Once-through high-pressure steam generator designed for steam-flood ing and recovery of the low-gravity, viscous oils of lower California.

Since produced crude is usually burned in the steam generators, the stack gases are scrubbed in wet scrubbers for removal of SO$_2$ and NO$_x$. Makeup to the scrubbers becomes concentrated and is usually treated with an antifoam and dispersant to minimize scaling, carryover, and restriction of gas flow that would interfere with furnace firing conditions.2

THE NATURE OF OIL FIELD WATERS

After establishing injection water quality, steps must be taken to eliminate or control scaling, corrosion, and fouling of surface equipment, tanks, and lines to prevent interruption of water injection or a decrease in oil production.

It is necessary to conduct several types of analyses to identify and evaluate these potential problems. Analyses must be run at points throughout the water system, because changes through the system provide data for proper control. The job of injection system control starts at the producing well, for it is here that water begins to change. As water enters the production tubing, a pressure drop occurs that in itself could cause precipitation either in the tubing string or in the formation. As the produced fluid approaches the surface, further pressure drop causes loss of gases and a reduction in temperature.

Substances in oil field waters are classified as: (1) dissolved ionic solids, (2) suspended solids, (3) dissolved gases, (4) problem-causing bacteria, and (5) residual oil.

Total Dissolved Solids (TDS)

In oil field brines, TDS ranges from less than 10,000 mg/L to over 350,000 mg/L, of which (NaCl) constitutes 80% or more. Troublesome cations found in oil
field waters are calcium (Ca); magnesium (Mg); barium (Ba); strontium (Sr); and ferrous iron (Fe). Commonly encountered anions are chloride (Cl), sulfate (SO\textsubscript{4}), bicarbonate (HCO\textsubscript{3}), and sulfide (S). Potassium (K), lithium (Li), boron (B), zinc (Zn), and copper (Cu) are also frequently measured. A few typical brine combinations are shown in Table 43.1. The "as calcium carbonate" designation, valuable to engineers working with surface waters, is virtually unknown in oil field water work. The standardized API report (Figure 43.17) includes both tabular and graphical forms.

### Suspended Solids

Various inorganic and organic solids are found in petroleum waters. These may be particles of metal oxides from well casings, or oxidized iron or manganese originally in the water. Other suspended solids may be silt, sand, clay, or bacterial bodies. These particulates are collected on a 0.45-μm membrane filter for identification. The filtered solids are analyzed separately (Figure 43.18). A high concentration of Freon-soluble extractables usually indicates the need for better demulsification or clarification of the water to be injected. Hydrochloric acid soluble materials include carbonates of calcium, magnesium, and iron, as well as oxides and sulfides of iron. Residue remaining after treatment could include silica, barium sulfate, calcium sulfate, or heavy hydrocarbons such as asphaltenes, which are insoluble in most solvents. The residue could also include bacteria.
## Dissolved Gases

The gases of greatest concern are hydrogen sulfide (H₂S), carbon dioxide (CO₂), and oxygen (O₂).

Produced waters containing hydrogen sulfide are called sour waters. Oil reservoirs can become sour through the activity of sulfate-reducing bacteria in the producing formation. H₂S concentrations can reach several hundred milligrams per liter. In many areas of the country elaborate mechanical systems are used to remove this gas from the produced water before reinjection.
As H\textsubscript{2}S is extremely poisonous, all sour oil field operators post conspicuous signs at tanks or vessels cautioning against inspection without the use of breathing equipment.

H\textsubscript{2}S in contact with iron produces iron sulfide, which can accelerate corrosion or act as a serious plugging agent. The sulfides of most metals are insoluble in water.

H\textsubscript{2}S can also be produced in the water handling system by sulfate-reducing bacteria. Any increase in H\textsubscript{2}S concentration through the water system not caused by blending is considered an indication of bacterial activity.

H\textsubscript{2}S in contact with dissolved oxygen can produce elemental sulfur, also a serious plugging agent.

\[
\text{H}_2\text{S} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{S}^\circ
\]

\textit{Carbon dioxide (CO\textsubscript{2})} is an ionizable gas, forming weak carbonic acid when dissolved in water. It is one of the greatest contributors to production well and waterflood system corrosion. Production well concentrations of CO\textsubscript{2} can exceed 200 mg/L, much of which is lost to the atmosphere when the produced fluids leave the well. Carbon dioxide is also responsible for dissolving limestone reservoir rock, increasing hardness and alkalinity.

\textit{Dissolved oxygen (DO)} is rarely present in produced fluids coming from the reservoir, unless entrained through leakage, but it is perhaps the most serious corrodent participating in oil field water corrosion mechanisms.

It is also responsible for creating plugging agents through oxidation of ferrous iron and hydrogen sulfide. It is important to try to exclude oxygen from all vessels, casings, and surface supply lines.

\textbf{Problem-Causing Bacteria}

Of several types of bacteria responsible for corrosion or production of plugging type solids, the most serious offender is the anaerobic sulfate-reducing bacterium, \textit{Desulfovibrio desulfuricans}. Historically these bacteria have been identified through the serial dilution or “extinction” dilution technique. The disadvantage of this technique is that a time lapse of 7 to 30 days might result before positive determination is made.

Using a new technique, bacteria filtered onto a pad from a water sample (0.45-\mu m filter) are immediately immersed in boiling water containing a buffer solution that destroys the enzymes which would normally consume ATP (adenosine triphosphate) upon cessation of life. The preserved ATP is reacted with luciferin and luciferase enzymes in a photometric cell, and the photons of light produced indicate total bacteria population within minutes after sampling.

\textbf{Residual Oil}

For a qualitative determination of residual oil, Freon extraction followed by weighing is recommended. This procedure requires time, limiting its use for monitoring.

A field procedure involving extraction of crude with chloroform gives good information concerning changes in oil concentration throughout the water system. In many cases, qualitative correlation with laboratory extraction methods is
quite close. The chloroform-extracted hydrocarbon is compared to prepared standards in a simple photometer. This method is restricted to use with crudes having a definite color.

MINERAL SCALES

The mineral scales of greatest concern to oil producers are calcium carbonate, calcium sulfate, and barium sulfate. Strontium sulfate, a less common scale, can also cause problems. Several iron compounds are also of concern, related to corrosion or to oxidation of ferrous iron as a consequence of oxygen intrusion. Table 43.2 lists common scales with system variables that affect their occurrence.

Mineral scales can form in many areas; supersaturation can occur in the formation face as the produced fluids enter the production tubing; scale can form throughout the length of the production tubing, on sucker rods, and in downhole pumps; it can form in surface vessels and on the heating surfaces in the heater treater. In the water handling system, scale can form in injection water pumps, surface lines leading to injection wells, and rock surfaces in the injection formation.

Some scales can be removed by chemical treatment, an expensive, time consuming process. Scales such as barium sulfate, which cannot be removed chemically, may require replacement of surface lines or abandonment of the well.

Calcium Carbonate

Calcium carbonate equilibria are frequently upset in oil field waters, because of changes in temperature, pressure, and pH. Because calcium carbonate solubility decreases with increasing temperature, injection from the surface to a warm formation increases the chance of calcium carbonate deposition. Its solubility

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formula</th>
<th>Primary variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium carbonate (calcite)</td>
<td>CaCO₃</td>
<td>Partial pressure of CO₂, temperature, total dissolved salts</td>
</tr>
<tr>
<td>Calcium sulfate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gypsum (most common)</td>
<td>CaSO₄·2H₂O</td>
<td>Temperature, total dissolved salts, pressure</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>CaSO₄</td>
<td></td>
</tr>
<tr>
<td>Barium sulfate</td>
<td>BaSO₄</td>
<td>Temperature, total dissolved salts</td>
</tr>
<tr>
<td>Strontium sulfate</td>
<td>SrSO₄</td>
<td></td>
</tr>
<tr>
<td>Iron compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferrous carbonate</td>
<td>FeCO₃</td>
<td>Corrosion, dissolved gases, pH</td>
</tr>
<tr>
<td>Ferrous sulfide</td>
<td>FeS</td>
<td></td>
</tr>
<tr>
<td>Ferrous hydroxide</td>
<td>Fe(OH)₂</td>
<td></td>
</tr>
<tr>
<td>Ferric hydroxide</td>
<td>Fe(OH)₃</td>
<td></td>
</tr>
<tr>
<td>Ferric oxide</td>
<td>Fe₂O₃</td>
<td></td>
</tr>
</tbody>
</table>
increases as the total dissolved solids content increases. For instance, the addition of 200,000 mg/L NaCl increases CaCO$_3$ solubility by over 100%. Prediction of calcium carbonate scale potential has been the subject of much research. The Langelier saturation index attempted to relate calcium and alkalinity concentrations to pH, temperature, and total dissolved solids. But this had limited value in oil field brines.

The Stiff-Davis index is now widely accepted for predicting calcium carbonate deposition in oil field systems. To be useful, the analytical data must be determined on freshly drawn samples; analyses determined in a laboratory are not reliable since the character of the water may change substantially. The Stiff-Davis index ranges from $-2.0$ to $+2.0$. Positive numbers indicate a progressively severe supersaturation; negative numbers indicate an undersaturated solution. The validity of the index depends on the accuracy of the analysis.

**Calcium Sulfate**

Most calcium sulfate deposits found in the oil field are gypsum (CaSO$_4$ · 2H$_2$O), the predominant form at temperatures below 100°F (38°C); above this temperature anhydrite (CaSO$_4$) may be found. Gypsum solubility increases with temperature up to about 100°F, and then decreases with increasing temperature. Sodium chloride increases the solubility of anhydrite, as it does for calcium carbonate, up to a salt concentration of approximately 150,000 mg/L. Higher salt concentrations decrease calcium sulfate solubility. The addition of 150,000 mg/L NaCl to distilled water triples the solubility of gypsum.

One of the more recent predictive indexes for gypsum is that developed by Skillman, McDonald, and Stiff. Calcium sulfate precipitation usually results from the mixing of two waters, one of which has a high calcium or sulfate concentration. A solubility graph relating calcium and sulfate concentration to total brine concentration is shown in Figure 43.19.

**Barium Sulfate**

Barium sulfate solubility is the lowest of the usual scales, approximately 2.3 mg/L in distilled water. The solubility of barium sulfate is also increased by increasing salt concentration. The addition of 100,000 mg/L NaCl to distilled water increases the solubility of barium sulfate from 2.3 mg/L to approximately 30 mg/L at 77°F (25°C).

The solubility of barium sulfate increases with temperature so that the combined effect of temperature and sodium chloride concentration can increase solubility to approximately 65 mg/L at 203°F (95°C).

Barium sulfate deposition usually results from the mixing of a barium-rich water with a sulfate-rich water. Such a combination should be avoided, but where mixing is unavoidable, chemical inhibitors may control deposits.

**Scale Prevention**

The first scale inhibitors were the inorganic polyphosphates, but their limitations were quickly discovered: above 140°F (60°C) they revert to orthophosphate, as they do at acidic pH or over a long residence time. The orthophosphate form does
Instructions for using the graph:

1. Determine concentrations of Ca (as CaCO₃), SO₄ (as Na₂SO₄) and Cl (as NaCl).
2. Plot the intersecting point of Ca and SO₄ concentrations on the graph.
3. If point lies above the diagonal line for NaCl level, the water will tend to precipitate CaSO₄. If point falls below the NaCl diagonal, the water is undersaturated and should not precipitate CaSO₄.

FIG. 43.19 Calcium sulfate solubility graph at various brine levels.

not inhibit scale. Present day oil field scale inhibitors are of three types: (1) esters of polyphosphoric acid, (2) phosphonates, and (3) organic polymers, such as polymers or copolymers of acrylic or methacrylic acid.

The phosphate ester formulations are versatile for most oil field water applications. Phosphonates and polymer products have definite advantages where water temperatures exceed 200°F (90°C). Dosages vary with temperature and the concentration of suspended solids, since solids adsorb the inhibitor, requiring higher concentrations for effective inhibition. Dosage is also directly proportional to the degree of supersaturation.

When applying scale inhibitors to producing wells the “squeeze” technique is frequently used. This involves injection of a scale inhibitor into the producing formation through the production tubing string under pressure. The scale inhib-
itor molecules adsorb to the formation, to be gradually released with the produced fluids. Scale inhibitor squeeze applications can last for periods up to 6 months. The need for renewed treatment is determined through tests for inhibitor residual in the produced fluids.

CORROSION

The primary corrodents in oil field water systems are carbon dioxide (CO₂), hydrogen sulfide (H₂S), and oxygen (O₂).

One reason oxygen is corrosive, even at low concentrations, is its participation in creating differential cells beneath deposits on metal surfaces, which become anodic to adjacent deposit-free areas. Control of oxygen corrosion in oil field water systems requires a conscientious effort to exclude air from all surface tanks and vessels and from the casings of producing wells. Field gas is used to maintain a positive gas blanket in these areas whenever possible.

After establishing control over oxygen exposure, it is then practical to use an oxygen scavenger to react with trace quantities of remaining oxygen. Several types of sulfite are used, including sodium bisulfite (NaHSO₃), ammonium bisulfate (NH₄HSO₃), sodium sulfite (Na₂SO₃), and sulfur dioxide (SO₂).

The chemistry is the same with all of these: the sulfite reacts with oxygen to form a sulfate ion.

\[ \text{SO}_3^{2-} + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_4^{2-} \]  

The sulfite-oxygen reaction is influenced by temperature and pH. Optimum pH for quick reaction is above 7. Most oil field waters will range in pH from 6.0 to 7.5.

Catalysis of the reaction is necessary. Sometimes naturally occurring metal ions in the produced water will do the job, but usually the catalyst is provided in the sulfite formulation.

In high-oxygen freshwater systems, passivating inhibitors such as chromate supplemented by zinc and phosphate may provide an alternative to oxygen scavenging. However, the presence of H₂S or certain easily oxidized hydrocarbons in injection systems reduces chromate and precipitates zinc, so these alternatives are seldom applicable in waterfloods.

Hydrogen sulfide is corrosive because it ionizes to form a weak acid:

\[ \text{H}_2\text{S} \rightarrow \text{H} + \text{HS}^- \]  

Whenever H₂S is present, iron sulfide deposits. These deposits are cathodic to base metal, so it usually follows that severe pitting occurs beneath iron sulfide deposits, all as a consequence of the H₂S. Where O₂ intrudes into a sulfide system, the rate of corrosion can become uncontrollable. Carbon dioxide mixed with H₂S is also much more aggressive than either of the gases alone. Where H₂S is present, an efficient film-forming inhibitor must be used to prevent severe, localized corrosion.

Invariably, corrosion inhibitors used in oil field water work are organic film formers. The molecules adsorb onto metal surfaces to shield the metal from the corrodents. Since the film-forming corrosion inhibitors must be added to a wide range of brine concentrations and in many cases to a mixture of water and hydrocarbon, inhibitors with a wide range of solubilities must be available. In the pro-
ducing well where a mixture of crude oil and brine must be treated, an inhibitor that is oil soluble and only slightly water dispersible is often required. This will film metal from the oil phase, providing long-term persistency to the metal surface; that is, the film will be maintained even when the inhibitor feed is discontinued. This allows batch treatment of producing wells in many instances. One of the most common methods of treating producing wells is using a treating truck to pump inhibitor down the tubing or into the annulus, followed by an overflush of produced water. The application is repeated periodically at intervals depending on the aggressiveness of the corrodents.

In injection water systems where water is the predominant phase, inhibitors must be either totally water soluble or highly water dispersible to carry through the surface line and tubing system. These inhibitors are not persistent, and it is necessary to feed continuously, always maintaining a residual in the system. Loss of inhibitor residuals results in desorption of inhibitor film and loss of protection.

In monitoring the chemical program, inhibitor residuals are determined through field extraction tests for close control.

Corrosion monitoring is usually accomplished through a combination of metal weight-loss specimens, corrosion meters, pipe spools or nipples (which have the advantage of duplicating flow conditions), and "iron counts." Residual iron concentrations are valid in systems without hydrogen sulfide. Where H₂S is present, iron is deposited as iron sulfide.

**BACTERIA CONTROL**

Control of bacteria is important in oil field water operations because they can cause plugging of the injection water formation or serious corrosion.

The most troublesome of these organisms is the anaerobic sulfate-reducing bacterium, *Desulfovibrio desulfuricans*. Present in many oil-bearing formations, it is involved in the chemical changes which occur during the formation of petroleum. It reduces inorganic sulfate (SO₄²⁻) to sulfide (S²⁻), which leads to iron sulfide precipitates.

*Clostridia*, another anaerobic sulfate-reducing organism, is not as prevalent as *Desulfovibrio*. This organism is reported to be thermophilic, preferring a temperature range of 55 to 70°C.

Several species of aerobic bacteria are also important, most of which are found in surface waters used to supplement produced water in a water flood. Some of the more important organisms are *Pseudomonas*, *Flavobacterium*, *Aerobacter*, *Escherichia*, and *Bacillus*. These form slime masses, which can cause plugging or which shield the anaerobic *Desulfovibrio*.

Iron bacteria are occasionally found in some water floods, the two major species being *Sphaerotilus* and *Gallionella*. These oxidize the ferrous ion (Fe²⁺) to ferric ion (Fe³⁺). Iron bacteria are identifiable through a microscopic analysis following staining.

*Beggiatoa* oxidize sulfide to sulfate. *Beggiatoa* usually grow in open produced water systems where a gathering line dumps into an open pit. They are often responsible for filter plugging.

Microbes are controlled by chemical application. The concentration of chemical and the period of contact varies among systems. Normally, chemical is fed at a selected dosage, such as 50 to 100 mg/L, for a period of 4 to 8 h. Following
application, samples are withdrawn from the system and microbial population is determined. The frequency of biocide application is dictated by such control tests.

In many situations, physical system cleanup is necessary to gain proper microbial control. Low spots in lines or tanks with bottom accumulations of sediment or debris protect bacteria from chemical contact. In these cases, the chemical program must be supplemented by a thorough “house cleaning.”

**SUGGESTED READING**

American Petroleum Institute: *Primer of Oil and Gas Production*, 1983.