## Physical and Chemical Properties of Reservoir Fluids

# I. OVERVIEW OF RESERVOIR FLUID CONTENT

a. Introduction
   i. Dominant Subsurface Fluids within 15,000 – 20,000 ft of Earth Surface
      1. Water – most abundant, predominant
      2. Oil and gas – relatively low volumes comparatively
         a. Oil and Gas occur in water-rich environment
         b. Water an important component of oil and gas exploration
   ii. Water-Oil-Gas mixtures and chemical properties vary according to regional geology
   iii. Oil and Gas
      1. Relatively insoluble in water; gas and oil are miscible with one another
         a. Gas dissolution / exsolving from solution
      2. Lower density than water
      3. Buoyant fluids
      4. NAPLs – Non-Aqueous Phase Liquids

b. Source of Data
   i. Drill holes and wells
      1. Drilling recovery, well cuttings, drilling mud, core
      2. Drill stem tests / fluid recovery
      3. Directly drill-hole sampling
   ii. Direct fluid sampling via wells
   iii. Borehole Geophysical measurements
      1. E.g. conductivity, resistivity
   iv. Reservoir fluid analysis over production life of well
      1. Changing dynamics as production wells are utilized

c. Fluid Distribution
   i. Controlling Factors
      1. Reservoir Porosity and Permeability
      2. Stratigraphic and Structural Relationships
      3. Density and Buoyancy Effects of Water, Oil, Gas
      4. Anomalous Lensing Possible (e.g. gas trapped below oil)
   ii. Layered Fluid Occurrence
      1. Gas less dense (on top) ----- Oil ------ Water Most Dense (on bottom)
      2. Oil-Water Table Contact vs. Gas-Water Table Contact
   iii. Interstitial Water
      1. Distribution of water in pore spaces throughout reservoir
         a. Range 10 – 30 %, up to 50%
   iv. Oil-Gas-Water Separation Process Necessary as part of well-head processing

# II. FORMATION WATER

a. Overview
   i. Oil Field Water
      1. “bottom water” or “edge water”
      2. Higher density brine water at base of oil and gas occurrence

b. Classification
   i. Meteoric – shallower groundwater, circulated from atmosphere
      1. Relatively low salinity
      2. Oxygen isotope signature
      3. High oxidizing potential and acidic
      4. Dissolved carbon dioxide + humic acids in  near surface environment

ii. Connate – long residence time, reservoir waters; “fossil water” removed from atmospheric circulation
    1. “Formation Waters”
    2. Characterized by high salinity brine waters
        a. Ionic sodium, postassium,chloride; bromine, calcium, magnesium (mobile cations)
        b. Sulfates, nitrates, and carbonates
        c. Reducing and alkaline in general

iii. Mixed – mixed connate and meteoric water
    1. Brines and salt common in oil
    2. Water forms hydration sheath in pore openings, separating oil and gas from pore walls

c. Characterization
    i. Water Saturation: percentage of effective reservoir pore space filled with water
        1. Measured by laboratory analysis
    ii. Salinity / total dissolved solids
        1. Measured via borehole geophysics, conductivity, resistivity
    iii. Depth Relations
        1. Zone 1: 0-1 km depth, meteoric water, stable salinity, oxidizing
        2. Zone 2: 1-3 km depth, salinity increasing with depth and residence time
        3. Zone 3: >3 km, reducing environment, hydrocarbon development
        4. Zone 4: depth > 5 km, incipient metamorphism, heat + pressure

d. Oil Field Brines / Connate Water
    i. Salinity Ranges (parts per thousand, g solute per L of water)
        1. Ocean Water average ~35 ppt (3.5%)
        2. Meteoric Water / “Fresh Water” < 1 ppt
        3. Oil Field Waters: ranges up to ~300 to ~500 ppt (30-50%)
        4. >salinity with > depth and residence time in subsurface
    ii. Brine Water Salinity and Chemical Composition Greatly Varies with Geology of the Oil Basin
        1. Reservoirs characterized by unique brine water compositions
    iii. Sources of Salinity
        1. Long residence times in formation, dissolution of reservoir framework
        2. Ion exchanges with clay minerals
        3. Evaporation / concentration of formation waters in depositional environment
        4. Original composition of marine waters at time of deposition

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## Measuring concentrations of solutes in aqueous solutions

**Concentration** - measurement of the quantity of solute in a given quantity of solvent (or solution)

**Mass Percent** = (mass solute / total mass solution) * 100%   (percent = "parts per hundred" (%)

E.g. if 5 g of NaCl is dissolved in 95 g of water, what is the mass percent of sodium chloride in the solution? (conversion factors for mass: 1 gram = 1000 mg, 1 kg = 1000 g, 1 gram = 1,000,000 Micrograms)

**Parts per Thousand** (o/oo) = grams of solute / liter of water

Determine the concentration in ppt for a solution of 200 gram dissolved in 2 liters of water? Determine the concentration in ppt for a solution of 2000 mg dissolved in 1 liter of water?

**Parts per Million** = milligrams of solute / liter of water

Determine the concentration in ppm for a solution 20 mg of salt per liter of water? What about 20 kg of salt per liter of water?

**Parts per Billion** = micrograms of solute / liter of water

Determine the concentration in ppb for a solution of 200 micrograms of salt dissolved in 3 liters of water?
Determine the concentration in ppb for a solution 200 grams of salt dissolved in 4 liters of water?

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## III. CRUDE OIL

a. Overview
   i. Small percentage of total fluids in reservoir rocks (dominated by water)
   ii. Crude Oil = liquid oil hydrocarbons
      1. Variable in composition and physical properties
      2. Dependent upon source rock composition and geologic history
      3. Mixtures with dissolved gas and free gas
      4. Soluble in organic solvents
   iii. Solid petroleum

b. Measurement
   i. Volume measurements:
      1. barrels, tons, acre-feet
      2. 1 barrel = 42 gallons (US); avg.wt. = 310 lbs
      3. Abbreviation for "barrel" = bbl
   ii. Oil recovery
      1. Pumped from wells into separator tanks
      2. Gas, oil, water separated
      3. Pumping and storage rates regulated and gaged

c. Chemical Properties
   i. Comprised of over 200 organic compounds
   ii. Gas, oil, asphalt = primarily hydrocarbons, with minor sulfur, nitrogen, oxygen

**Average Elemental Composition by % Weight**

| Element | Crude Oil | Asphalt | Natural Gas |
|---|---|---|---|
| Carbon | 82-87 | 80-85 | 65-80 |
| Hydrogen | 12-15 | 8.5-11 | 1-25 |
| Sulfur | 0.1-5.5 | 2-8 | tr – 0.2 |
| Nitrogen | 0.1-1.5 | 0-2 | 1-15 |
| Oxygen | 0.1-4.5 | -- | -- |

   iii. Molecular Composition – complex variety of over 200 organic compounds due to the versatile nature of carbon bonding with 4 electrons in outermost valence shell
      1. Hydrocarbon Compunds in Petroleum

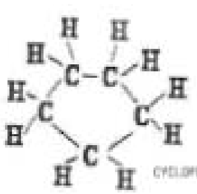
         a. Paraffins (alkanes) – saturated hydrocarbons, all C-H bonds satisfied by single covalent bonds
            i. General formula: $C_nH_{2n+2}$
               1. n < 5 gaseous at normal temp and pressure

2. n ranging from 5-15 liquid at surface temp. and pressure
3. n > 15 solid waxes and viscous liquids
4. box-chain hydrocarbon molecules
5. Common Examples in Petroleum
    a. Methane $CH_4$ (simplest)
    b. butane $C_4H_{10}$
    c. Pentane $C_5H_{12}$
    d. Hexane $C_6H_{14}$
    e. Octane $C_8H_{18}$

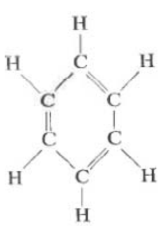
METHANE

ii. stable bonds, less reactive hydrocarbons
iii. complex variability of bonding combinations in hydrocarbon family

b. Napthenes (cycloparaffins)
    i. General formula: $C_nH_{2n}$
    ii. Liquid at normal temperatures and pressures
    iii. Branching ring-shape hydrocarbon molecules
    iv. Comprise ~40% of crude oil composition
    v. Common Examples in Petroleum
        1. Cyclopentane $C_5H_{10}$
        2. Cyclohexane $C_6H_{12}$



c. Aromatics (benzene series)
    i. Ring shaped hydrocarbon molecules
    ii. E.g. common in petroleum: benzene $C_6H_6$



Benzene, $C_6H_6$
Mol. wt. 78.11
B.P. 80°C

d. Complex Residues – Asphaltics
    i. High molecular wt., solid to semi solid
    ii. Petroleum residue
    iii. High in sulfur, oxygen, nitrogen

2. Mixed compounds / other constituents
    a. Crude oil contains low percentages of oxygen, nitrogen, sulfur, trace metals
    b. Sulfur occurs as free S or dissolved hydrogen sulfide gas H2S
    c. "sour crude", degrades quality of petroleum for use
        i. <0.5% low sulfur crude
        ii. >0.5% high sufur crude
    d. Nitrogen – low amounts in crude, inert constituent in natural gas
    e. Oxygen – minor component
    f. Organic matter, fossil materials, microscopic, mixed as solids in crude oil
3. Average Organic Composition of Crude Oil

| **Molecular Type** | **Weight Percent** | |
|---|---|---|
| Paraffins | 25 | |
| Napthenes | 50 | |
| Aromatics | 17 | |
| Asphaltics | 8 | |
| | Total | 100 |

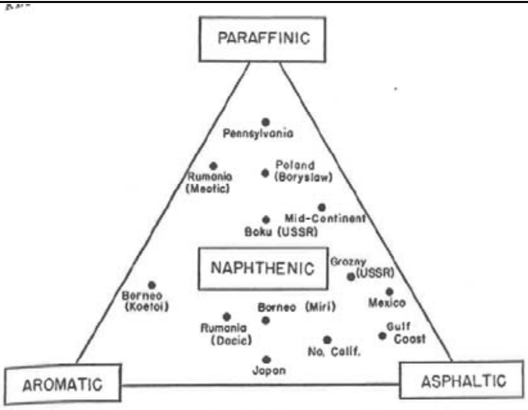



FIGURE 5-19 *The relations of constituents of various crude oils.* [*Redrawn from Gruse and Stevens,* Chemical Technology of Petroleum, *2nd ed (1942), pp. 6 and 7, Figs. 1 and 2.*]

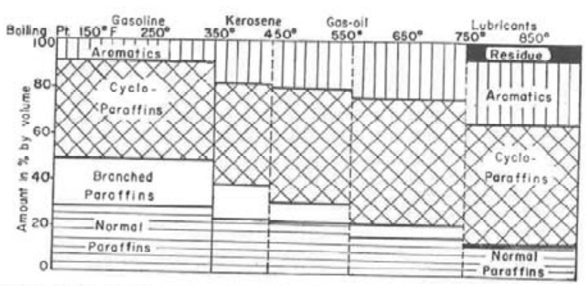



FIGURE 5-22 *The percentage composition by volume of the chief products obtained from United States crude oils.* [*Redrawn from Shaffer and Rossini Proc. Amer. Petrol. Inst., Vol. 32 (1952), p. 64.*]

d. Physical Properties of Crude Oil
    i. Density
        1. Mass density = mass / volume

2. Specific Weight = weight/volume = (mass)(g)/volume
    a. g = acceleration due to gravity = 9.8 m/sec$^2$
3. Specific Gravity = mass density of substance / mass density of water
    a. Temperature dependent
    b. Dimensionless ratio, units cancel
4. Volume a function of temperature: heat energy and kinetic molecular energy
    a. > temp, > volume; directly proportional
5. American Petroleum Institute (API) Gravity Index Classification
    a. High API gravity values = low specific gravity, Low API gravity values = high specific gravity
    b. API 10 = density of water, API values > 10 = floaters; API values < 10 = sinkers

API GRAVITY INDEX EQUATION:

$$\text{Degrees API} = \frac{141.5}{\text{S.G. at } 60^{o}\text{F}} - 131.5$$ where S.G. = specific gravity of oil sample

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Example, given an oil sample with a density of 900 kg/m3 and density of water of 1000 kg/m3 at a given temperature, calculate the API gravity index for the oil sample.

S.G. = $D_{oil}$ / $D_{water}$ = (900 kg/m$^3$) / (1000 kg/m$^3$)= 0.9

Degrees API = [141.5 / (0.9)] – 131.5 = 25.7

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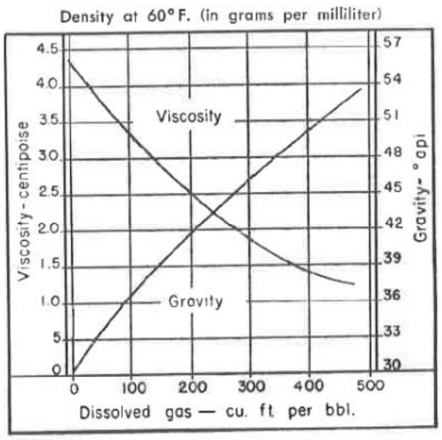
c. API Gravity Classification of Oils
    Light Oil – API > 31.1
    Medium Oil – API between 22.3 and 31.1
    Heavy Oil – API < 22.3
    Extra Heavy Oil – API < 10.0
d. API Gravity Range of Crude Oil on average 15-57 degrees
    i. Varies according to source region, geology

ii. Volume – pressure dependent
1. Gas commonly dissolved in oil within reservoir at depth, under high pressure
2. Extraction of oil results in < pressure and temperature at surface
    a. Gas exsolves from oil as it reaches surface, net fluid volume decreases in remaining liquid (“inflated oil”)
    b. 1 barrel oil in subsurface = 0.8 barrel at surface (shrinkage factor)
3. > Depth, > Pressure, > capacity for dissolution of gas in oil

iii. Viscosity
1. Measure of fluid resistance to flow
    a. High viscosity – thick liquid, highly resistant to flow; vice versa
2. Range: Liquid oil and gas; Plastic petroleum compounds
    a. Highly variable range in viscosities
    b. Temperature dependent; > temp < viscosity, < temp > viscosity
    c. > gas content < viscosity; < gas content > viscosity




d. Measurement using a rolling ball viscometer; relative index
    i. Units: poise (p) and centipoises (cp)
    ii. Viscosity ranges
        1. Water = 0.894 cp
        2. Motor oil 40W = 319 cp
        3. Tar = 2.3 x $10^{11}$ cp

iv. Optical Properties
    1. Reflectance – measurement of the degree to which light is reflected from organic matter
        a. Vitrinite – immature organic matter, derived from lignin and cellulose in plant material
        b. Vitrinite Reflectance – predictor of petroleum potential in source rock, a measure of thermal maturation
            i. Calibrated to reflectance of crude oil; Ro index = 1.0 (fully mature hydrocarbarbon)
                1. Ro >0.8 thermally mature organic matter, in oil and gas present
                2. Ro < 0.55 thermally immature organic matter
                3. Ro 0.55-0.8, organics in petroleum/gas producing range

    2. Refractive index
        a. Measurement of refraction or bending of light as it passes through an oil sample
        b. Measured as an index compared to transmission light through air; the higher the density, the more angle of refraction, the higher the index of refraction
        c. Refractometer – petroleum R index average ~1.4 compared to air

    3. Fluorescence – petroleum fluoresces under black light (Ultraviolet radiation)
        a. Useful test for petroleum occurrence in drill cuttings

v. Other Properties
    1. Color, smell
    2. Flash and boiling points – temperature at which petroleum vaporizes and flash-flames
    3. Coefficient of expansion and volume change upon heating / cooling
    4. Heat Content / Calorimeter Values
        a. Heat Potential / Measurement

i. calorie – the heat required to raise one gram of water, 1 degree Celsius
ii. KiloCalorie (used for food labels) = 1000 calories
iii. British Thermal Unit – amount of heat necessary to raise the temperature of 1 lb of water by 1 degree Fahrenheit
1. 1 BTU = 252 calories = 0.252 Kcal

b. Crude Oil ~ 19,000 BTU per lb
i. Variable controlled by hydrocarbon composition and geology, degree of thermal maturation

c. Bituminous Coal ~13,000 BTU per lb
i. Variable controlled by composition and geology, degree of coal development

## IV. NATURAL GAS

a. Components and Classification
i. Low-boiling point hydrocarbon gases
1. Range: small percentage dissolved in oil up to 100% of hydrocarbon fluids
ii. Mode of Occurrence
1. Free Gas (free product)
a. Common to occur as free gas cap over oil, and water
2. Gas Dissolved in Oil
a. Under subsurface pressures, gas dissolves in oil
b. Range: a few cubic feet up to 1000's of cubic feet per barrel of oil
c. Gas exsolves from oil as it reaches the surface
i. Gas-water-oil separation at well head
ii. Flaring disposal vs. capture, depending on economics
3. Gas Dissolved in Water
a. Natural gas dissolved in oil field brine waters; up to 20 cu. ft / bbl of water
b. Lower solubility in water, compared to oil (6% comparatively)
4. Liquified Gas
a. High pressure conditions > 5000 psi
b. Liquified gas resemble oil in liquid state

b. Measurement of Natural Gas
i. Volumes =
1. Measured in cubic feet or millions of cubic feet Mcf
2. Temperature and Pressure Dependent
a. Ideal Gas Law PV = nRT

$$PV = nRT$$

where *P* is the pressure of the gas, *V* is the volume of the gas, *n* is the amount of substance of gas (measured in moles), *R* is the ideal, or universal, gas constant, and *T* is the temperature of the gas.
P = pressure in atm    V = Volume in liters    n = mass in moles    T = temperature in degree Kelvin
R = 0.0821 liter-atm/$^{o}$K-mole

3. Formation Pressures: 1000's of PSI range, decrease with production

c. Composition –
i. comprised mostly of Paraffins (alkanes)
1. Methane $CH_4$ (simplest and most abundant)
2. butane $C_4H_{10}$ (low percentage)
3. Pentane $C_4H_{12}$ (low%)
4. Hexane $C_6H_{14}$ (low%)

ii. Classification
    1. Dry gas vs. Wet gas (content of liquid vapors)

d. Impurities / additional gas mixtures: hydrogen sulfide, nitrogen, carbon dioxide
    i. Helium – derived as part of radioactive decay process in minerals
    ii. Hydrogen Sulfide – problematic from a processing standpoint, corrosion agent