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1. Learning Outcome:

After studying this module you shall be able to:

- Know about necessity of studying oil field water, definition of free, interstitial water and oil field brine
- Learn about different classification schemes of oil field water and graphical methods used for representation of complex chemistry of oil field waters
- Understand how study of oil field water help as a lead in hydrocarbon exploration and repairing of a damaged well.

2. Introduction:

In most cases sedimentary rocks are deposited under water and hence are, inherently water-wet. Thus irrespective of composition of sediments, water becomes an integral part of any sedimentary unit as it occupies the pore spaces within the sediment. In course of burial and diagenesis, much or all of this entrapped water either get altered in composition, get partially displaced by other fluids viz. oil, gas etc. or are expelled altogether. The water that oil or gas is able to displace is referred to as '*free water*'. However, waters held in very fine pore spaces are known as '*interstitial water*' and resist displacement by other fluids because of high capillary pressure in very narrow pore throats. As such, interstitial water comprises 10-40% or even more of the total pore space.

Each water-bearing formation contains water that is chemically different from waters in other horizons. Hence, the chemical quality of formation water in an oil- and/or gas-bearing region is very important for exploration and exploitation in an area. During exploration for oil/gas, the composition of formation water can depict if a favorable trap is available and whether that would contain the oil/gas. While, the confined oil/gas traps contain only connate water, some traps, in general, and shallow traps, in particular, may come under the influence of 'fresh' water, technically termed as meteoric water. In this case, the flowing meteoric water may result in the flushing of the oil/gas accumulation from the trap, resulting in the trap devoid of any oil/gas. In addition, presence of meteoric water, which is generally oxygeneted, lead to the degradation of oil. And hence, the composition of the formation water in terms of meteoric and/or connate, can depict the probability of having oil/gas accumulation in the trap. During exploitation of oil/gas, if an oil or gas well suddenly starts producing water, a chemical analysis can depict from which horizon it is coming. This is the most important reason for oilfield water analysis as it helps both in identification of the water source horizon as well as repairing of the damaged well.

Further, the composition of formation water can give idea on physical presence of oil/gas even if a favorable trap is available. While, any confined oil/gas trap contains only connate water, some traps, in general, and shallow traps, in particular, may come under the influence of 'fresh' water, technically termed as meteoric water. In this case, the flowing meteoric water may result in the flushing of the oil/gas accumulation from the trap, resulting in the trap devoid of any oil/gas. Further, meteoric water oxygenate and lead to the degradation of oil. Hence, composition of formation water in terms of meteoric and/or connate, can depict the probability of having oil/gas accumulation in the trap.

3. Chemistry of Oil field waters:

Chemical analysis of Oil field water is carried out by the use of methods standardized by American Petroleum Institute (API). Commonly, oil field waters are analyzed for five major components viz. Ca^{+2}, Mg^{+2}, Cl^-, HCO_3^-, SO_4^{-2}. Content of another cation e.g Sodium (Na^+), which is common in oil field brine, is identified by means of difference as it is difficult to analyze on regular basis.

It is known to us from basic chemistry that each element or radical has its own combining weight; e.g., to form NaCl, 22.997 grams of Na^+ react with 35.457 grams of Cl^-, no more or no less. In fact, the sum of equivalent weights of cations must equal to the sum of equivalent weights of anions. The equivalent weight of an ion is obtained by multiplying the actual weight of an ion (expressed as milligram per liter) by its valency and then dividing the product by atomic or molecular weight of the ion. For Formation water analysis, it is advantageous to express the analyses in milliequivalents per liter because equal numbers represent equal combining weights.

$$\text{meq/l} = \frac{\text{mg/l x valency}}{\text{molecular weight}}$$

In analytical results from laboratories concentrations of cations and anions in Formation brine are commonly shown in terms of parts per million by weight (ppm). For our understanding it is preferable to express the results in terms of milligrams per liter (mg/l) using the following relationship:

$$\text{mg/l} = \frac{\text{ppm}}{\text{density}}$$

We assume that the three anions viz. Cl^-, HCo_3^- and SO_4^{-2} constitute nearly 99% of Formation brine and contributions of other anions viz. iodides, bromide, carbonate only minimum. In some rare cases Similarly, it is considered that the cations positive ions are all Na^+, Ca^{++} and Mg^{++} . However, this is often not true as it is reported that many Formation brines are also rich in K^+, Sr^{++} and Ba^{++}. Analyses of these cations are done separately.

4. Classification of oilfield waters:

4.1 Genetic classification:

On the basis of origin and subsequent history, subsurface waters are classified into three classes viz. Meteoric, Connate and Juvenile. Normal sea water contains 3.5% (35,000ppm) dissolved solid, whereas most oilfield brines contains much more solid in dissolution i.e., as high as 300 000ppm or more. Commonly formation waters with total solid content 10% (100 000ppm) are referred as *brine*.

Meteoric water: Meteoric waters are those which presently form part of hydrologic cycle or remained part of it in recent geological past. These include the oceanic water, water evaporated in the atmosphere, water in rain and snow, surface water and ground water in motion. Chemically, meteoric waters are characterized by low concentration of dissolved solids; usually less than 10,000 mg/l. Meteoric waters are rich in bicarbonate (HCO_3^-) ions.

Connate Water: The word ‘Connate’ means ‘born with’ i.e. water remains of original sea in which sediments were deposited. This is only partially true as compaction of sediments expel large amount of pore water depositionally trapped within sediments. Immovable waters held by high capillary force within fine pores and water released from clay minerals in course of diagenetic recrystallisation add on to the connate waters. As such, buried waters, which remained segregated from the hydrological cycle for considerable period of time in geological past are referred to as Connate water. Chemically connate waters are very salty, containing 20,000 to 250,000 mg/l total dissolved solid. They are high in chloride, but bicarbonate is scarce or absent. Sulfate content is also limited or absent in these waters.

Juvenile Water: Waters which have ascended from the mantle of the Earth and have never taken part in the hydrologic cycle are referred to as Juvenile water. However, Juvenile waters are hard to identify as most waters escape from volcanoes are ground waters which are vaporized by the hot lava. Water from hot springs and geysers are not juvenile water but meteoric water, which on percolation through fractures got heated up by high temperature at depth.

4.2 Chemical classification:

There are two schemes of chemical classification of oil field waters a. on the basis of salinity and alkalinity; and b. depending on the dominant mineral ions present in solution.

a. *on the basis of salinity and alkalinity (Palmer, 1911)*

It is defined that the strong bases (Na^+, K^+) are combined with strong acids (Cl^-, SO_4^{-2}) to form *primary salinity*. The strong bases are combined with weak acids (HCO_3^-) to form *primary alkalinity*.

Further, combination of weak bases (Ca^{+2}, Mg^{+2}) with the strong acids (Cl^-, So_4^{-2}) form secondary salinity and combination of weak acids (HCO_3^-) with weak bases (Ca^{+2}, Mg^{+2}) form secondary alkalinity.

This scheme of classification lost its luster since combinations of ions as proposed in the scheme do not take place and it became hard to relate different water classes to their history and geology.

b. On the basis of *dominant mineral ions present in the solution (Sulin, 1946)*

Under this scheme waters are distinguished as of four major classes depending on the distribution of three cations and three anions as illustrated in the following table (Table I)

Table I: Oilfield water classes according to Sulin classification

Class of water	Types of water	Ratios of concentrations expressed as milliequivalent percent

		$\frac{Na}{Cl}$	$\frac{Na-Cl}{SO_4}$	$\frac{Cl-Na}{Mg}$
Meteoric	Type a: Sulfate-sodium	>1	<1	<0
	Type b: Bicarbonate-sodium	>1	>1	<0
Connate	Type c: Chloride- Magnesium	<1	<0	<1
	Type d: Chloride-Calcium	<1	<0	>1

Most oilfield waters belong to type d where Na^+ is present as cation besides Mg and Ca. Chloride is almost the sole anion. Formation waters of this type are found in deep, stagnant basins in continental interior where surface waters have no access to the formation. Type c waters characterize evaporite-bearing sequences.

In contrast, meteoric waters (Types a and b) contain SO_4^{-2} and HCO_3^- but very little Ca and Mg. Na^+ is the sole cation. These water types are found in near-surface artesian conditions. In particular, waters containing bicarbonate and sulfate are oxygen-bearing, sub-saline and in some cases almost of fresh water character.

If it is assumed that Na^+ is the only cation present then the sum of milliequivalent percents of anions must nearly equal Na^+

$$Na^+ = Cl^- + SO_4^{-2} + HCO_3^- \text{ (approximately)}$$

$$Na^+ - Cl^- = SO_4^{-2} + HCO_3^- \text{ (approximately)}$$

If the ratio (Na-Cl)/SO_4 is less than one, waters are classified as Type a (sodium-sulfate), whereas if the value comes as more than one the water is designated as of type b (bicarbonate-sodium). In both these classes of water Na/Cl ratio will be more than one.

Connate waters do not contain sulfate or bicarbonate and thus the only anion present is chloride. Hence,

$$Cl^{-} = Na^{+} + Ca^{+2} + Mg^{+2} \text{ (approximately)}$$

$$Cl^{-} - Na^{+} = Ca^{+2} + Mg^{+2} \text{ (approximately)}$$

If the ratio Cl-Na/Mg is less than one, then the water is classified as type c (chloride-magnesium). In contrast, if the value of Cl-Na/Mg comes more than one it will be type d (chloride-calcium). However, in both type c and type d Na/Cl value will be less than one.

Under this scheme waters are classified by plotting them graphically. The Na-Cl difference measured in meq is plotted up if it is positive and down if it is negative. Further, if the difference is positive, the Mg is plotted to the right of the origin. If it is negative, the SO_4 is plotted to the left of origin. Plotting of a number of water samples is shown in Fig.1.

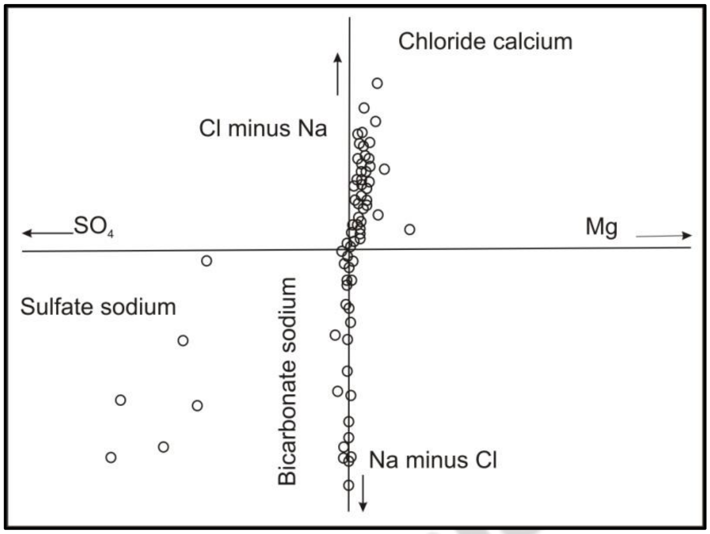

Fig. 1 Sulin classification of oilfield waters. Plotting of number of oil field water samples are shown in the figure as open circles.

5. Application of water analysis data:

For geological purposes and as an exploration lead it is often advantageous to show water analysis data on the map, preferably on the isochore map. The most popular method for plotting of chemical analysis data of water samples is the Stiff diagram (Fig. 2). In stiff diagram the chemical data (in milliequivalent) are plotted on a logarithmic scale and hence, there is no zero. Any value that is less than one meq is plotted as one. Cations are plotted in the diagram to the left from the center on three or four lines and anions are plotted to the right. The plotted points are connected by straight lines and the polygon so formed is made colored/blackened.

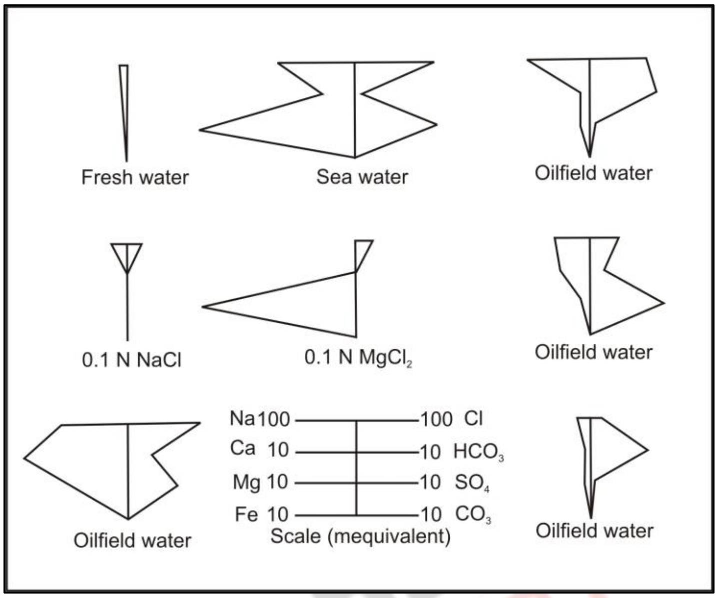

Fig. 2 Common patterns of Stiff diagrams for 0.1 N Nacl, fresh water, sea water and oil field waters (after North, 1985).

Now for better understanding, let us assume two water analysis data of two different oil fields as shown in Table II. While water 1 is typical connate water, water 2 is meteoric in origin. The stiff diagrams thus formed for connate and meteoric water samples following Table I are as under:

	Factor valence		*Water 1*			*water 2*	
Element	*mole. weight*	*mg/l*	*meq*	*meq%*	*mg/l*	*meq*	*meq%*
Na^+	0.0435	44,100	1,918	74	3,040	132.2	99
Ca^{++}	0.0499	11,000	549	20	21	1.0	0.5
Mg^{++}	0.0823	1,500	123	6	7	0.6	0.5
Total cations			2,590	100		133.8	100
Cl^-	0.0282	91,800	2,589	100	3,240	91.4	68.3
SO_4^{--}	0.0208	none			407	8.5	6.3
HCO_3^{--}	0.0164	34	0.5		2,065	33.9	25.3
Total anions			2,590	100		133.8	99.9

Table II: Chemical analysis data of Water 1 (Connate) and water 2 (meteoric)

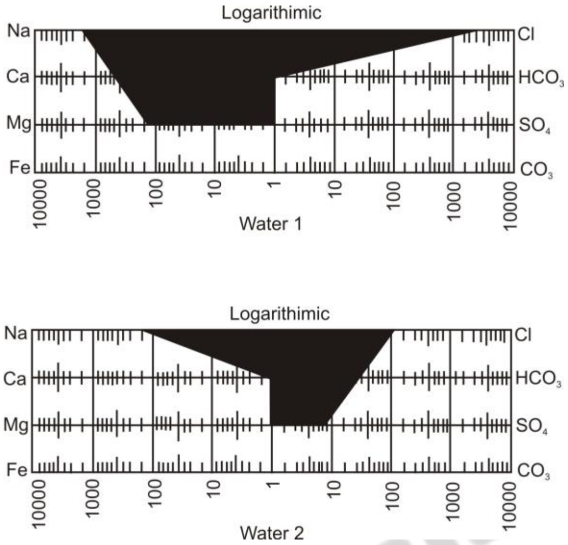

Fig. 3 Characteristic stiff diagram patterns for Connate (water 1) and meteoric (water 2) waters.

Fig. 4 illustrates a map on which water qualities in the form of stiff diagrams from a subsurface reservoir are plotted graphically. Although the reservoir strata is concealed in the subsurface in most parts of the map; its exposures can be seen in the western and southeastern flanks of the map. While in the western flank it exposes at an elevation of 3200ft, in the southeast of the map its exposure is seen at much lower elevation i.e at 1200 ft. As wells drilled in the central part of the map yielded water, it was assumed that water enters the outcrop in the west and issues in the east.

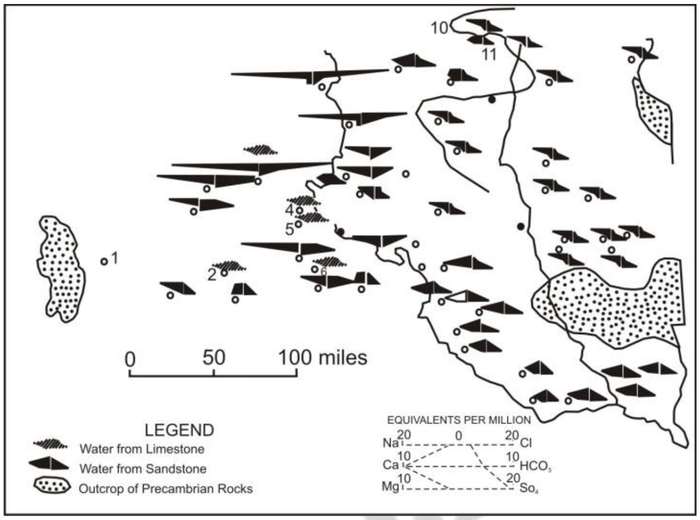

Fig. 4 Water quality data from a subsurface reservoir are plotted graphically on a map using stiff diagrams (modified after Dickie, 1986).

However, the water analysis data from the area did not support the above conjecture. It is noticed that water quality in the eastern part of the map is different from water quality in the western part and hence, it is presumed that waters from eastern and western parts of the map cannot be components of same hydraulic system. This gave birth to further high-resolution exploration in the area and it was found that the reservoir strata is lenticular in character in the western part of the map although it becomes permeable in the eastern part. Further, it was ascertained that water enters not through the reservoir strata but through the cavernous limestone strata. This limestone subcrops on the unconformity that is overlain by the reservoir strata (Fig. 5). Limestone water everywhere is high in bicarbonate, sulfate and calcium. While waters from the reservoir strata in the eastern part of the map are chemically similar with limestone waters; in western parts of the map reservoir waters are rich in sodium and chloride and low in bicarbonate. Water analysis thus provided the lead for exploration and helped in i) understanding reservoir geometry and ii) delineating a subsurface unconformity.

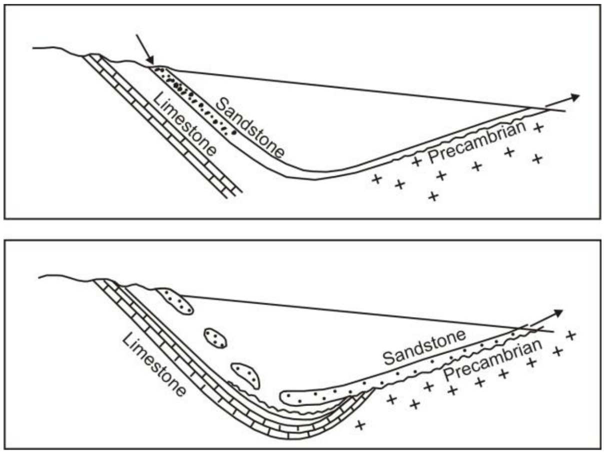

Fig. 5 Subsurface model for a reservoir bed before (upper) and after (lower) water analysis. According to revised model water enters through limestone and discharge into the reservoir sandstone along its subcrop (modified after Dickie, 1986).

6. Summary:

On the basis of mode of occurrence, sub-surface waters of oil fields are broadly classified into two categories viz. Free water and interstitial water. Interstitial water is also referred to as *irreducible water* as it cannot be replaced by any other fluid (oil or gas) in course of subsequent diagenetic history of sediments. Oil field waters contain varying concentrations of inorganic salts. Waters containing more than or equal to 100,000ppm TDS are referred to as *Brines*. As such, oil field waters are alkaline and strongly reducing. Genetically subsurface waters are classified as meteoric, connate, and juvenile. Meteoric waters differ from connate waters not only in salinity but also in chemistry. While meteoric waters have high concentrations of bicarbonate and sulfate as anions, in connate waters chloride represents the major anion along with Na^+ as major, if no sole, cation. Stiff diagram is an useful way for graphical representation of these complex compositional variability of subsurface waters, which often helps in terms of exploration and exploitation.

FAQs:

Q1. What do we refer by 'free water' and 'interstitial water' in a hydrocarbon reservoir?

Ans: Water forms an integral part of any sedimentary unit as it occupies the pore spaces within the sediment. Through burial and diagenesis, much or all of this entrapped water either alter in composition, get displaced by other fluids viz. oil, gas etc. or expelled altogether. The water that oil or gas is able to displace is referred as *'free water'*. However, waters held in very fine pore spaces are known as '*interstitial water'* and resist displacement by other fluids because of high capillary pressure in very fine pore throats.

Q2. How do we classify oil field waters chemically and represent these chemical data?

Ans: Oil field waters are analyzed for five major components viz. Ca^{+2}, Mg^{+2}, Cl^{-}, HCO_3^{-}, SO_4^{-2}. It is assumed that the sum of equivalent weights of cations must equal to the sum of equivalent weights of anions. The equivalent weight of an ion is obtained by multiplying the actual weight of an ion (expressed as milligram per liter) by its valency and then dividing the product by atomic or molecular weight of the ion. For Formation water analysis, it is advantageous to express the analyses in milliequivalents per liter because equal numbers represent equal combining weights.

$$\text{meq/l} = \frac{\text{mg/l x valency}}{\text{molecular weight}}$$

The most popular method for plotting of chemical analysis data of water samples is the Stiff diagram. In stiff diagram the chemical data (in milliequivalent) are plotted on a logarithmic scale and hence, there is no zero. Any value that is less than one meq is plotted as one. Cations are plotted in the diagram to the left from the center on three or four lines and anions are plotted to the right. The plotted points are connected by straight lines the polygon so formed is made solid. The stiff diagrams for connate and meteoric water samples can be as follows:

Q3. Enumerate classification of oil field waters on the basis of salinity and alkalinity. Discuss merit/demerit of this classification scheme?

Ans: This classification scheme is based on the presumption that the strong bases (Na^+, K^+) are combined with strong acids (Cl^-, SO_4^{-2}) to form *primary salinity* and the strong bases are combined with weak acids (HCO_3^-) to form *primary alkalinity*.

Further, combination of weak bases (Ca^{+2}, Mg^{+2}) with the strong acids (Cl^-, So_4^{-2}) form secondary salinity and combination of weak acids (HCO_3^-) with weak bases (Ca^{+2}, Mg^{+2}) form secondary alkalinity.

This scheme of classification lost its luster since combinations of ions as proposed in the scheme do not take place and it became hard to relate different water classes to their history and geology.

Q4. Define 'Sulin' classification. How can we differentiate connate and meteoric waters using this scheme of classification?

Ans: In Sulin classification, geochemical ratios viz. Na/ Cl, (Na-Cl)/ SO_4, (Cl-Na)/Mg and distribution of three cations viz. Na, Ca and Mg are taken into consideration for classification of waters. Waters are distinguished as of four major classes as illustrated in the following table.

Types of water	Ratios of concentrations expressed as milliequivalent percent		
	$\frac{Na}{Cl}$	$\frac{Na-Cl}{SO_4}$	$\frac{Cl-Na}{Mg}$
Type a: Sulfate-sodium	>1	<1	<0

Meteoric				
	Type b: Bicarbonate-sodium	>1	>1	<0
Connate	Type c: Chloride- Magnesium	<1	<0	<1
	Type d: Chloride-Calcium	<1	<0	>1

Most oilfield waters belong to type d (connate) where Na^+ is present as cation but both Mg and Ca are present in addition with Ca: Mg ratio being 5:1. Chloride is almost the sole anion. Formation waters of this type are found in deep, stagnant basins in continental interior where surface waters have no access to the formation. Type c waters characterize evaporite-bearing sequences.

In contrast, meteoric waters (Types a and b) contain SO_4^{-2} and HCO_3^-but very little Ca and Mg. Na^+ is the sole cation. These water types are found in near-surface artesian conditions. In particular, waters containing bicarbonate and sulfate are oxygen-bearing, sub-saline and in some cases almost of fresh water character.

Q5. 'Salinity (TDS) of oilfield waters increase with depth' - Do you consider it as an unequivocal statement? If not, why?

Ans: Yes, salinity of oil filed waters normally increase with depth as oils normally gets lighter with depth. However, there may be exception to this general rule i.e both hydrologic and oil density profiles are reversed (Fig. 6). In such instances, the lower density of water at depth is represented by reduced contents of Na^+ and Cl^- ions. We normally observe this kind of phenomenon in thick, deltaic sequences with multiple sand reservoirs deposited in a transgressive regime and followed by a regression. In such situation brackish water sands get overlain by marine sands and each sand having its own oil/water contact. It is probable that for any single bed the situation is normal i.e going down the dip of a bed the oil density decreases but across the sequence of reservoir beds the hydrologic and oil profile seems reversed, although the changes never smooth but abrupt. The underlying figure illustrates the situation.

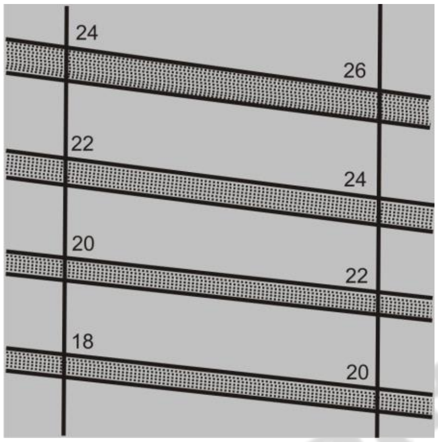

Fig. 6 Reversed oil gravity profile in Baku Oil field (after North, 1985)

Suggested Readings:

1. North F. K (1985). Petroleum Geology, Kluwer Academic Publishers. ISBN: 0045530041, 978-0045530045.
2. Selley, Richard C. and Sonnenberg, Stephen A., (2014). Elements of Petroleum Geology, 3rd Edn., Academic Press. ISBN: 978-0-12-386031-6
3. Dickey, Parke A. (1981). Petroleum Development Geology, 2nd Edn., Pennwell Publishing Co. ISBN: 087814174X, 978-0878141746.