

IDENTIFICATION OF NANOTECHNOLOGICAL PROCESSING IN THE OIL DEBIT

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Today, oil companies' activity is associated with difficult technological problems as about 2/3 available oil and gas resources are referred to hard-extractive resource category. High costs of their extraction technology reduce their profitability. Developed countries of the world spend many funds for oil science development and it enables to generate high-rentable technologies for extraction of hard-extractive oil resources. Therefore, it should be noted that mechanism of oil displacement from oil polls to producing wells is to be studied in-depth.

Oil-saturated beds are represented as porous materials with different size of pores, pore channel and material systems of rocks specifying features of interaction of bedded and injection fluids and rock. Subject to the noted above, it may be concluded that oil displacement from oil pools to producing wells is not a mechanical process of oil replacement with water, but a complex physical-chemical process at which ion exchange process between bedded and injection fluids and rock [1, 2], i.e. nano-size processes play the key role.

Mechanism of oil travel in bed and its extraction is mainly formed by molecular - surface (nano-size) processes taking place in phase boundary. Therefore, the wettability matter is one most important issues of nanoscience on oil extraction, mechanism modelling of which is the subject of our researches.

It should be noted under in-place conditions, there are contacts between two and three phases in large aggregations of capillary channels where mutually insoluble liquids (oil and water) move. In such contacts, selective wetting of hard phase surface with water and oil is different (see figure 1), therefore, meniscuses forming capillary pressure (CP) are formed. CP for spherical surface of meniscus according to Laplace law can be determined by the following formula :

$$P_{\sigma} = (2\sigma_{12} / r) \cos \theta \quad (1)$$

where r is capillary radius (K_n)

Complete wetting meets unlimited liquid spreading on the surface of solid body being, thereby, spontaneous esoteric process i.e. always accompanied by decrease in free energy to every following 1 cm^2 of the wetted surface. Such decrease, also called as spreading coefficient :

$$-dF / dS > 0(\sigma_{23} - \sigma_{12}) = \beta - \sigma_{12} \quad (2)$$

Should, thereby, be positive :

$$-dF / dS > 0(\sigma_{23} - \sigma_{12}) = \beta > \sigma_{12},$$

where β is wetting energy.

Complete wetting condition i.e. energy decrease when water 1 displaces oil 2 early contacted with the solid body surface 3 would be more, i.e.

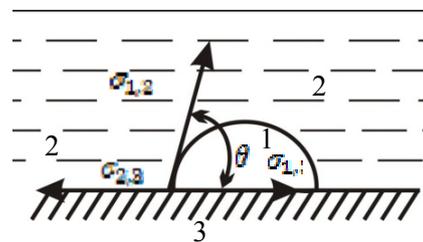


Figure 1. Drop shape based on surface tensions in different boundaries of contacting phases.

$\sigma_{1,3}$, $\sigma_{1,2}$ and $\sigma_{2,3}$ are surface tensions in phase sections 1-3, 1-2 and 2-3; 1-water; 2 – oil or gas; 3 – solid body; θ - wetting angle

$$(\sigma_{23} - \sigma_{13}) - \sigma_{12} > 0 (\beta > \sigma_{12})$$

When such spreading condition is not met, i.e.

$$-\frac{dF}{dS} = (\sigma_{23} - \sigma_{13}) - \sigma_{12} < 0$$

Water 1 together with the surface 3 forms finite contact angle (θ):

$$\frac{(\sigma_{23} - \sigma_{13})}{\sigma_{12}} = \cos \theta = B, \text{ where } +1 \geq B \geq -1.$$

In such cases, CP absorbing forces is always less than its maximum value

$$(P_{\max} = 2\sigma_{12}/r) \text{ and is } (P_{\sigma} = 2\sigma_{12}/r)\cos \theta = P_{\max} \cdot B$$

Only while wetting energy is positive ($\beta > 0$, though less σ_{12}) CP will be towards the absorbing side, that is $\theta < 90^\circ$, i.e.

$$0^\circ \leq \theta < 90^\circ, \quad +1 \geq B > 0, \quad P_{\max} \geq P_{\sigma} > 0$$

When θ is $> 90^\circ$, i.e. in the case of negative wetting energy $\beta = \sigma_{23} - \sigma_{13} > 0$, CP changes sign ($0 > B \geq -1$), $P_{\sigma} > 0$), passing through zero and becomes buoyancy force preventing water intrusion to its nonwetable K_n , especially at low penetrability.

Studies carried out by us have shown that CP, the value of which depends of the section surface features specified many capillary (nano-size) effects sufficiently affecting motion of oil, water and gas in oil collector (C).

If water wets the C rock, then CP will be motive factor when oil is displaced by water.

If water doesn't wet the surface of rock part, then CP is inhibitive factor to be overcome when oil is displaced by water.

The role of capillary forces in processes taking place in the bed when oil is displaced is reasonable to be followed by C simplified model of the oil bed (figure 2) represented as two cylindrical capillaries (K_n) 1 and 2 connected each other by both ends. Both K_n have the same length but K_n 1 radius is more that K_n 2 one. Both K_n

are primarily filled K_n with oil and water motion is from A to B. At first, we'll consider the case when oil is displaced by water from K_n , the walls of which are hydrophilic (figure 2, a).

As water wets K_n , then meniscuses in the boundary of the water – oil section will be seen so as it is shown in figure 2 and, therefore, it will be displaced by water from both K_n . According to (1) the pressure in K_n 1 will be

$$P_{k1} = (2\sigma_{12} \cos \theta)/r_1 \quad (3)$$

The pressure in capillary 2

$$P_{k2} = (2\sigma_{12} \cos \theta)/r_2 \quad (4)$$

where σ_{12} are the surface tension in the boundary of the water – oil section; r_1 and r_2 are 1 and 2 capillary radiuses, accordingly.

As, according to the data $r_1 > r_2$, then $P_{k2} > P_{k1}$, and, therefore, oil affected by K_n forces should be faster displaced from K_n 2 than from K_n 1. Therefore, at the moment when water has passed through K_n 2, having displaced oil, not all oil will be displaced from K_n 1, its part will remain in pores. Due to inrush of water in K_n 2 into channel B connecting both C, such part of oil will be retained in K_n 1 pores. CP affecting such drop of oil from the left cannot

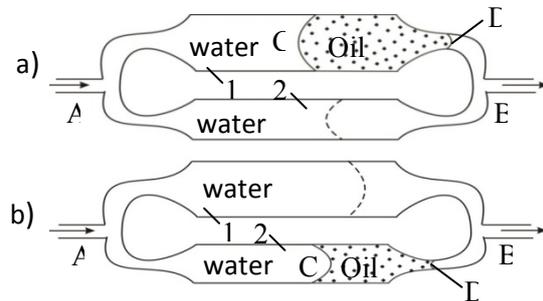


Figure 2. Oil ousting from oil collectors by water.

displace it as the meniscus curve in the boundary of water – oil section (C point) from the right is more than the meniscus curve (D point) from the left and, therefore, CP will be more from the right. Even in the case of sufficient increase in discharge pressure, trapped oil drop cannot be displaced as pressure differential (ΔP) falling along the length of an insulated drop is less than CP acting from the right. Finally, the pressure affecting the drop from the left (CP+ ΔP) is balanced by CP from the right and the oil drop sticks in C pores and it will be left beyond displacement front.

As opposed to the foregoing K_n , in hydrophobic C the forces are directed against motion of injected water (figure 2, b) and, therefore, some additional pressure of injected water is required to overcome CP. As $r_2 < r_1$, CP in $K_n 2$ is more than in $K_n 1$ and, therefore, water velocity in $K_n 2$ will be less. As a result, at the moment when water has displaced oil from $K_n 1$ and entered into channel B connecting output ends of both K_n in $K_n 2$, a part of oil will not be still displaced and be beyond displacement front.

In the intermediate wettability collector (at $\theta = 90^0$), water absorption under influence of K_n forces is sufficiently weaker than in the environment completely wetted with water. In such cases, K_n forces are not prevailing factor any more. Motion resistant forces may be in such correlation with K_n forces that water will move in both pores approximately at the same velocity in spite of different area of their cross section. In such case, oil is displaced from pores of different diameter at the same time and it should result in larger extraction of oil than in the cases of limit rock wettability by water or oil.

Studies carried out have shown that the C rock wettability by water not only affects the CP changes but also causes swelling (figure 3) and fragmentation of the C K_n internal surface and formation of colloidal system (suspension) - shaped clay particles resulting in the C K_n obstruction and decline in oil output. As it is shown in figure 3, the water layer is retained in the surface of clays by hydrogen bonds with the hex-shaped lattice of oxygen atoms.

The water entering into the clay crystal structure (the structured water) penetrates up to 10 m from the outside surface.

The structured water has very high viscosity (30 times higher) as compared with free water and generates rheological problems resulting in decrease of oil output.

As a result of molecular - surface phenomena (nano - size processes) in the boundary of the phase section of the oil bed, besides wettability, the adsorption process

of surface- active components (especially, pyrobitumens) of oil in rockforming minerals is of most importance. This process, first of all, is associated with hydrophibization of the surface and, therefore, decrease in recoverable oil. Formation of an adsorption layer results in construction of such layer-based boundary layer of oil, the viscosity of which is higher by an order than the viscosity of oil in volume, and the thickness, in most cases, is commensurable with the radius of pore channels. Bennett and Barton's work importance [3] should be especially noted, where it was determined that even at the presence of a film of water in the surface of a rock due to adsorption of surface - active components of oil, the film is broken and, as a result, hydrophobization of hydrophilic surface occurs.

In addition, in work [3], information about wettability of most deposits in many oil – producing regions of the world has been gathered. Laboratory researches have shown that 27%

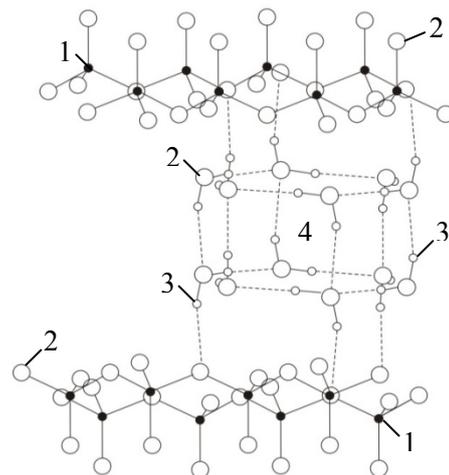


Figure 3. Adsorption layers of water between dehydrated clay beds. 1- Si^{4+} , Al^{3+} ; 2 - oxygen anions; 3 - hydrogen cations; 4 - hex-shaped cylindrical structure of water.

of layers studied are hydrophilic, 66% are hydrophobic and 7% have intermediate wettability. For carbonate rocks, the number of hydrophobic layers reaches 84%. At that, injected water in the bed is used ineffectively.

$$r_e = [(8V\mu\ell)/(\pi\Delta Pt)]^{1/4} \quad (5)$$

where V , μ is filtered oil volume and viscosity; ℓ is capillary length (see figure 2); ΔP is pressure differential; t is filtration time.

As follows from the aforesaid results of studies of (1-4) formulas and [4] Poiseuille's formula enabling calculation of the K_n effective radius under oil filtration, the C K_n nanotechnology processes can result in the C penetrability decrease and resistance increase and, therefore, decrease in oil output. However, such negative nano-effects may be prevented if appropriate reagents enabling to ensure intermediate wettability conditions ($\theta = 90^\circ$) are used for oil output control.

Conclusion

Nanotechnology processes have been identified in oil output. It has been shown that oil output process intensification is based on nano-size processes such as the collector rock wettability, deposits of surface – active components of oil in the surface of capillaries. The recoverable oil increase method has been suggested.

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