



Surface wettability control of reservoir rocks by brine

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Abstract: Based on adhesion models between rock surface groups and organic molecules, the interactions between the chemical groups on the rock surface and the components of crude oil and the interactions of the electrical double layers at the rock surface and oil-water interface were analyzed to investigate the abilities and microscopic mechanisms of wettability control by H^+ , OH^- and inorganic salt ions in brine, and a new method of wettability control for reservoir rocks was built. The results show that the interaction forces between rock surface groups and oil molecules are van der Waals forces, Coulomb forces, hydrogen bonds, and surface forces. By changing these forces, the control mechanisms of surface wettability of reservoir rocks by brine are: transformation of chemical groups, change of interfacial potential, pH variation of injected water, multicomponent ionic exchange, and salting-in or salting-out effect. For sandstone reservoirs, with the decrease of concentration and valence state of positive ions in brine or the increase of pH (increasing pH has a negligible impact on the brine salinity), the interaction between rock surface and oil becomes weak, thus resulting in increase of water wettability of rock surface. For carbonate reservoirs, $CaSO_4$ or $MgSO_4$ brine with high concentration is beneficial to increase water wettability of rock surface. Therefore, it is feasible to control rock wettability and improve oil recovery by adjusting the ion components of injected water.

Key words: rock surface; wettability; brine; intermolecular force; microscopic mechanism; enhanced oil recovery

Introduction

Wettability, a fundamental characteristic parameter of reservoir property, is an important factor affecting capillary force, microscopic sweep volume and residual oil saturation. Therefore, it is of great importance for effective development of oil reservoir to regulate the wettability of rocks. At present, the main chemical agent for regulating wettability is surfactant^[1–2]. Due to the special structure of them, surfactants have multiple disadvantages when used to regulate wettability. For example, they are usually expensive and sensitive to hard water, and have poor temperature resistance. They have absorption loss in the formation and negative impact on the environment. Besides, there are rigid requirements on their structure, concentration and dosage. Hence, it is of great significance to design a kind of high efficient, economic, temperature-resistance and salt-resistance and environment friendly chemical agent for regulating wettability.

Brine has been proved to be able to adjust the wettability of rock surface by a large number of lab and field tests. Nasralla et al. found that when decreasing the salt ion concentration of

the injected water or increasing the pH, the contact angle of water on the rock surface in the system of rock-brine-crude oil decreased, and the surface of rock turned from neutral to water-wet^[3]. Through imbibition experiments of cores in different kinds of brine, Hua et al. found that when Ca^{2+} concentration was increased, the imbibition rate of brine decreased greatly and rock surface became less hydrophilic; when the Ca^{2+} concentration or the salinity of the brine decreased, imbibition was more likely to happen and the rock surface became more hydrophilic^[4]. Rezaeidoust et al. proved that the combination of Ca^{2+} and SO_4^{2-} or Mg^{2+} and SO_4^{2-} could enhance the hydrophilicity of carbonate rock surface, accordingly, the imbibition ability of reservoir, which was helpful for increasing recovery efficiency of such kind of reservoirs^[5]. By analyzing log data of open wells, Vledder et al. demonstrated that decreasing the salinity of injected water could make the reservoir turn from mixed-wet or oil-wet to water-wet^[6]. The technology of adjusting the rock wettability and consequently enhancing oil recovery by controlling the ions of injected water has gained extensive attention abroad, and the flooding

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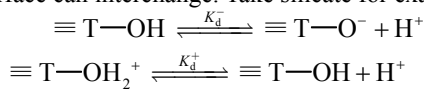
technology using low salinity water^[7] has been applied in Alaskan^[8], Snorre^[9–10], and the Middle East oil fields^[6, 11], etc. and has achieved remarkable effect.

In this study, the interaction forces between the groups on rock surface and organic matter are analyzed on the basis of eight adhesion models of rock-brine-crude oil to probe into the microscopic mechanism of adjusting rock wettability by brine, and to work out an approach to adjust rock wettability with brine. This study provides reference for formulating a scientific standard of ion components of the injected water, correctly understanding the rock wettability and exploring approaches for enhancing oil recovery.

1. Groups and wettability of reservoir rock surface

1.1. Chemical groups of rock surface

Sandstone reservoir rock or carbonate reservoir rock is mainly composed of silicate minerals or carbonate minerals of different crystal structures and properties. The main components of these minerals include quartz, feldspar, calcspar, dolomite and clay minerals (such as chlorite, the mixed-layer minerals of illite and smectite, kaolinite and illite). Microscopically, there exist different kinds of chemical groups at different number density on the rock surface. For example, quartz (SiO₂) belongs to atomic crystal, there are three different silanol groups ($\equiv\text{Si}-\text{OH}$, $\equiv\text{Si}-\text{OH}_2^+$, $\equiv\text{Si}-\text{O}^-$) on its surface with different electrical properties^[12]. The common chemical formula of feldspar is $\text{M}[\text{T}_4\text{O}_8]$ (M stands for K, Na and Ca elements, and T stands for Si and Al elements). Feldspar is a kind of silicate with shelf-shape, and its surface has silanol groups or aluminol groups ($\equiv\text{Al}-\text{OH}$, $\equiv\text{Al}-\text{OH}_2^+$, $\equiv\text{Al}-\text{O}^-$)^[13] with different electrical properties. Clay minerals like kaolinite ($\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$) and montmorillonite ($\text{Al}, \text{Mg}_2[\text{Si}_4\text{O}_{10}](\text{OH})_2 \cdot n\text{H}_2\text{O}$) etc. are also silicates with layer structure, and their surface have silanol groups or aluminol groups^[14–16]. Calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) are carbonates with island-shape, both ionic crystals with positive ion $\equiv\text{CO}_3\text{Ca}^+$ and negative ion $\equiv\text{CaCO}_3^{-17}$ mainly. The groups on rock surface can interchange. Take silicate for example:



Therefore, the density of the charged groups ($\equiv\text{T}-\text{O}^-$ and $\equiv\text{T}-\text{OH}_2^+$) is dependent on the concentration of H^+ ^[18–19] according to dissociation equation:

$$\sigma^- = f^- \sigma_0 = \frac{K_d^-}{K_d^- + [\text{H}^+]_\infty e^{-e\varphi_0/kT}} \sigma_0 \quad (1)$$

$$\sigma^+ = (1 - f^+) \sigma_0 = \frac{[\text{H}^+]_\infty e^{-e\varphi_0/kT}}{K_d^+ + [\text{H}^+]_\infty e^{-e\varphi_0/kT}} \sigma_0 \quad (2)$$

1.2. Wettability of rock surface

The chemical groups on rock surface have different electric quantity and polarity, and different interaction potential energy between them and liquid molecules, leading to different

wettability degrees of rock surface. A number of researchers measured the hydrophilicity of various minerals^[20]. They found that quartz and feldspar have stronger hydrophilicity, while carbonate minerals have weaker hydrophilicity. Because the electric charges on the silica tetrahedron sheet layer, the aluminum oxide octahedral sheet layer and the head face of clay minerals are imbalance, the surface of clay minerals has negative electricity and they are often regarded as cation exchange materials. Different clay minerals are different in crystal structure and construction unit, so they have different capability of cation exchange. Montmorillonite has the strongest capability of cation exchange, illite and chlorite are in the second place, kaolinite is the worst^[21]. The capability of cation exchange of clay minerals determines the adsorbing capacity of rock surface to positive ions in the water solution and polar components in crude oil, and further affects the rock wettability. Dubey et al. thought that the quartz surface under reservoir conditions was entirely hydrophilic^[22]. However, large amounts of charged clay minerals are usually adsorbed on the pore wall and have great effect on the rock wettability. For example, montmorillonite has strong capacity to absorb water, therefore, its existence can enhance the hydrophilicity of rock. In contrast, the existence of iron-containing clay minerals, e.g. $\text{Fe}_3\text{Al}_2\text{Si}_2\text{O}_{10} \cdot 3\text{H}_2\text{O}$, can make part of rock surface hydrophobic because iron can adsorb surface active materials in crude oil^[23].

2. Active components of crude oil and their interaction with rock-brine

2.1. Interfacial active components in crude oil

Petroleum is a very complex mixture with carbon and hydrogen up to 95% to 99% and heteroatoms (mainly sulfur, oxygen and nitrogen) ranging from 1% to 5%. Although the amount of sulfur, oxygen and nitrogen is very low, these elements exist in the form of hydrocarbon derivatives. For example, sulfur in crude oil mainly exists as mercaptans, thioethers, disulfides, thiophenes and their homologues. Oxygenated compounds, including naphthenic acids, fatty acids, phenols, anhydrides, ethers, esters, ketones, amides, and other compounds containing oxygen, are usually acidic or neutral; nitrogenous compounds, mainly including pyridine, quinoline, amine, carbazole, pyrrole and their derivatives, are generally alkaline or neutral^[24]. Therefore, the content of compounds containing sulfur, oxygen and nitrogen is much larger in petroleum. These non-hydrocarbon components are polar ingredients, and mainly exist in resin and asphaltene. With strong interfacial activity, they can change the wettability of mineral surface^[25]. One end of the molecules containing sulfur, oxygen and nitrogen are polar groups, which are adsorbed on the mineral surface by coulomb force or hydrogen bond, while the alkyl group in other end is exposed outside^[18], which leads to the enhancement of oil affinity of the rock surface. At different pH values, polar groups in non-hydrocarbon components can undergo protonation or deprotonation processes, which

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