

Adsorbed oil of gas condensate fields

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Abstract

The pore space of reservoir rocks has a lot of active centers capable to form different types of bonds (from hydrogen to chemical). Therefore, almost any hydrocarbon can be adsorbed to a particular extent on the internal pore surface and form an adsorbed layer, which has a definite spatial configuration and makes contact with a certain part of the rock surface. Study of gas condensate reservoirs brings up the question of the composition of adsorbed hydrocarbons. The properties of such hydrocarbons in many giant gas condensate fields are of special interest as these compounds can serve as an additional source of resources after production of mobile-gas reserves. The performed study of gas condensate reservoirs of the Karachaganak, Astrakhan, and Yamburg fields has shown that their adsorbed hydrocarbons (adsorbed oil) have polar components with sulfur and oxygen atoms.

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Introduction

Starting from the research by Durmish'yan (1963a,b, 1979), numerous studies have shown that the pores of many gas and gas condensate fields contain both irreducible water and residual oil. The latter decreases the efficient gas-saturated pore volume of a hydrocarbon (HC) pool. This leads to distorted results of assessment of gas reserves by the volumetric method. The highest discrepancy between the actual and assessed reserves was observed during analysis of the development of the Karadag gas condensate field (Durmish'yan, 1963b). Residual oil saturation (ROS) was for a long time considered an integral parameter of a reservoir. However, special studies of the structure and properties of residual oil showed that ROS is a complex dynamic system consisting of several types of residual oil: primary (not subject to the action of different processes), entrapped, adsorbed, film, of dead-end pores, unstable displacement, etc., which differ in physico-chemical properties and the mode of occurrence in pores (Mikhailov, 1992).

By now, only the experience in studying adsorbed water in grounds and other dispersed systems has been gained; there

is extensive basic research on this subject (Bobrov et al., 2015; Deryagin et al., 1989; Osipov et al., 2014; Raitburd and Slonimskaya, 1970; Zlochevskaya, 1969). Meanwhile, the properties of adsorbed HCs have been poorly studied.

Adsorbed oil is of special significance as it changes the reservoir wettability from hydrophilic to hydrophobic (Mikhailova and Sechina, 2013) and controls the distribution of fluids in the pore space (Kuzmin et al., 2013, 2015). The presence of adsorbed oil is due to adsorption of its surface-active components in the pores of reservoir rocks. Some giant gas condensate fields have large reserves of adsorbed oil (Mikhailov et al., 2012), but its properties in gas condensate reservoirs are still unstudied. Meanwhile, data on the composition and properties of adsorbed HCs bear valuable geological information, which is currently not used in geological prospecting or for the substantiation of the technologies of HC reserve recovery (Lavrent'ev et al., 2015; Mel'nikov et al., 2014; Schertl et al., 2015). This information can help to prolong production of huge HC reserves remained in the pool after the completion of its scheduled exploitation, which is urgent for the life of the Russian Far North cities focused on HC recovery. Therefore, the problem of study of the composition and properties of residual HCs is of crucial importance for increasing the efficiency of subsurface management (Ermilov et al., 2004).

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The reservoir energy depletion during the gas reserve recovery leads to the formation of liquid HC condensate, which, together with adsorbed oil, occupies part of the pore space. Its recovery is also of commercial interest. Note that the technologies of recovery of residual oil and HC condensate are radically different. Therefore, the physicochemical and technological properties of the condensate–adsorbed-oil system call for subsequent differential study both for the identification of the HC state in the reservoir and for the substantiation of the technologies of effective additional HC recovery from depleted gas condensate pools.

Factors affecting the sorption activity of hydrocarbons and rocks

Adsorption of HCs is driven by molecular forces, namely, dispersion forces (induced by deformation of atomic or ionic electron shells) and orientation forces (orientation of dipoles around the surficial adsorbent ions, i.e., in the pore space). Adsorption can occur via hydrogen bonds and depends on temperature and pressure. In situ adsorption is of mixed types (physical and chemical). It is possible both in static and in dynamic conditions.

The pore space of reservoir rocks has a lot of active centers capable to form different types of bonds (from hydrogen to chemical). Therefore, almost any hydrocarbon can be adsorbed to a particular degree on the pore surface.

The surface charges at the shears and protrusions of the rock pore space, in the corners and at the edges of the crystal lattice, and at the sites with isomorphic substitution of the lattice ions by lower-charge ions can serve as active adsorption centers (Galkin et al., 2015). On contact with the reservoir water, additional sources of charges appear at the rock surface. Depending on the solvent power of the reservoir water, the molecules of the solid surface can dissociate into ions, with one part of the ions passing into the reservoir water and the other part remaining bound to the solid surface and being an additional source of surface charge in the medium. Sometimes, crystal lattice is built up through adsorption of the solution ions having a high chemical affinity for the crystal lattice ions. “Superequivalent selective” adsorption of ions from the solution takes place, and an uncompensated charge arises, which favors adsorption of particular ions. In clayey rocks, specific adsorption of ions from the solution is possible via the Van der Waals (electrostatic) forces generated by the polarization of the surface atoms by adsorbed ions. The OH groups also participate in the formation of active surface centers. They are a component of the crystal lattice of most clay minerals and can exchange their hydrogen for metal ions (cations) under certain conditions (e.g., a pH increase) (Tarasevich and Ovcharenko, 1975). Thus, a lot of adsorption centers arise at the rock surface. Excess of surface ions of one sign (charge) drives the attraction or corresponding orientation of molecules of water and other polar substances of the opposite sign.

The sorption activity of rocks decreases in the series clays–siltstones–clayey sandstones–polymictic sandstones–dolomites–limestones–anhydrites (Mileshina et al., 1983).

Silicates usually have a negative charge and a weakly acidic surface, whereas carbonates have a positive charge and a weakly basic surface. Therefore, the former adsorb simple organic bases, whereas the latter adsorb simple organic acids, i.e., compounds of the opposite polarity (Anderson, 1987).

Adsorption of simple hydrocarbons

Hydrocarbons with polar chain molecules having one active center at the end of the chain (carboxylic acids, monatomic alcohols) are of vertical orientation. Horizontal orientation is specific for chain molecules having polar groups at both ends of the chain (dibasic fatty acids). If the active center of adsorbed HC molecule is in the middle of its chain, the molecule branches can be arranged at different angles with respect to the normal to the surface.

Nonpolar HC molecules, despite their strong difference from polar ones, are horizontally oriented relative to a solid surface and form adsorption films. The structure of HC in the subsurface layer is more ordered than those in the layers remote from the rock surface. The adsorption bond energy of HCs depends on the molecule structure and on the nature and structure of the adsorbent. Adsorption of olefins and aromatic HCs on silica gel is stronger than adsorption of naphthenes and paraffins. The adsorption bond energy depends on the presence of active (with respect to the adsorbent) centers in a HC molecule (in the case of silica adsorbent, these are aromatic cores and multiple bonds of HCs), on the total surface area occupied by the molecule, on the distance between the surface and carbon atoms, and on the most advantageous orientation of the molecules. Isoparaffins with the same number of carbon atoms as in other HCs have the weakest adsorption bond (Glembotskii, 1980). The above types of orientation are specific for particular molecules.

Natural HC mixtures are usually complex multicomponent systems. Their adsorption differs from that of one-component HC systems.

Adsorption in multicomponent hydrocarbon systems

Natural HCs are complex multicomponent phases of varying composition (Golovko et al., 2014).

In complex mixtures, such as a HC raw material, polar molecules are the first to be adsorbed. They are adsorbed by a polar surface group, thus neutralizing the surface charge. The first adsorbed layer (and, often, the second one too) is initially inhomogeneous: It consists of aggregates and molecules of different orientations. Then, an adsorbed layer resembling a bilayer membrane forms. The longer is the molecular chain, the stronger is adsorption, because the HC molecules are adsorbed by many segments. Chain branching hinders packing of molecules in the adsorbed layer and

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