EFFECTS OF PORE STRUCTURE AND WETTABILIT Y ON METHANE ADSORPTION CAPACITY OF MUD ROCK: INSIGHTS FROM THE ORGANIC MATTER/CLAY MINERALS MIXTURES

P. Luo¹, N.N. Zhong¹, Z.P Guo¹

¹ China University of Petroleum, China

Introduction

The pore structure of shales has a notable effect on methane adsorption capacity and usually is positively correlated with the methane adsorption capacity (Clarkson et al., 2013). Organic matter (OM) is the main contributor for methane adsorption (Chalmers and Bustin, 2008). The clay minerals also have large specific surface area and abundant nanopores, and thus provide an important supplement to methane adsorption sites (Ji et al., 2012). However, the micropore structure of Fort Simpson shales is controlled by the clay minerals content although there is a positive correlation between TOC and methane adsorption capacity (Ross and Bustin, 2009). So the positive effect of pore structure on methane adsorption capacity of mud rock has to be further investigated.

Wettability, defined as the affinity of a rock to a particular fluid, largely depends upon rock mineralogy and properties of the materials coating the rock surface (Anderson, 1986). The wettability of OM is of great difference from that of clay minerals. Previous studies show the wettability of OM-hosted pores tends to be more oil-wetting, whereas inorganic pores (e.g., pores in clay minerals) are often water-wetting (Yassin et al., 2017).

Methane adsorption capacity of OM always predominates the clay minerals adsorption capacity and the co-existence of OM and clay minerals within shales makes it difficult to assess their individual adsorption capacities (Ji et al., 2012; Tan et al., 2014). Therefore, previous studies on methane adsorption capacity of shales usually discussed the OM and clay minerals capacities separately (Heller and Zoback, 2014; Ji et al., 2012; Kuila and Prasad, 2013).

In the present study, artificial samples consisting of organic matter (anthracite, type II kerogen) and clay minerals (kaolinite, montmorillonite) are prepared in different proportions to investigate: (1) variation in methane adsorption capacity and pore structure when OM and clay minerals are mixed with different proportion; (2) the relationships of pore structure and wettability with methane adsorption capacity; (3) competitive methane adsorption of OM and clay minerals. The results will provide new insights into methane adsorption and also do help to estimate the adsorbed methane of OM and clay minerals under reservoir conditions.

Results

Methane adsorption isotherms from the mixed samples are in accord with Langmuir model and the methane adsorption capacity of OM is higher than that of clay minerals. From nitrogen adsorption isotherm analyses, pore structure parameters including specific surface area and pore volume of OM are lower than that of clay minerals showing that the methane adsorption capacity of mixed samples is primarily controlled by organic matter content and are inversely related to the specific surface area and pore volume. This makes the organic matter content a more reliable parameter than pore structure to evaluate methane adsorption capacity.
Wettability experiments were performed using contact angle, liquid-liquid extraction and spontaneous imbibition methods. The result of wettability for OM and clay minerals shows that OM is hydrophobic and clay minerals are hydrophilic. Methane as an organic fluid, is more preferentially to be adsorbed on OM instead of clay minerals. During methane adsorption, well developed pores in clay minerals are not as effective as those in OM, which leads to an inevitable methane adsorption competition between OM and clay minerals in mixed samples.

Conclusions

The pore structure, methane adsorption capacity and wettability characteristic of mixture samples including clay minerals and OM in varied OM content to illustrate effects of pore structure and wettability on methane adsorption capacity of mud rock. The following conclusions were reached:

(1) The methane adsorption capacity of OM is stronger than that of clay minerals, though specific surface area and pore volume of clay minerals are larger than those of OM in mixed samples. It is because the OM pores are hydrophobic while clay mineral pores are hydrophilic, which leads to the preferential adsorption of methane on OM than clays.

(2) Instead of pore structure, wettability may be the key parameter to determine the methane adsorption capacity between OM and clay minerals. The well-developed inorganic pores in mud rock may not represent high methane adsorption capacity.

(3) Methane may be preferentially adsorbed on the surface of OM at subsurface where moisture is always existing and mostly occurs around the hydrophilic clay minerals.

References