Water Effect on Methane Adsorption in Shale Through Kerogen by High Pressure Methane Adsorption

Wei Li[1], Colin Snape[1], Lee Stevens[1], Ling Tang[2]
[1]Faculty of Engineering,University of Nottingham; [2]State Key Laboratory of Petroleum Resources and Prospecting

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Abstract

Shale gas has attracted increasing attention. 20-85% shale gas adsorb on kerogen and clay surface in shale. Water plays an important role in gas adsorption. Recent studies about water effect is mainly focused on clay minerals rather than kerogen. Thus, it is vital to know water effect on gas adsorption on kerogen in shale for better estimating shale gas resource. Kerogen is not only the material basis of gas generation but also can provide space for gas storage. Two (N1, N2) kerogen samples are isolated from shale by demineralization. Wet kerogen and shale samples are created under 95% relative humidity (RH) condition. Brunauer-Emmett-Teller (BET) specific surface area (SSA), and Horváth-Kawazoe (H-K) micropore volumes of shale and kerogen are determined from CO2, and N2 adsorption isotherms at 0℃ and -196℃. High-Pressure Methane adsorption (HPMA) experiment up to 105bar are carried out at 25 °C on dry and wet samples. The BET results show the SSA of wet N1 and N2 kerogen are 22 and 14 m^2/g, which are much smaller than dry kerogen, 143 and 145 m2/g. The SSA of dry N1 and N2 shale are reduced from 25 and 19 m2/g to 0.15 and 0.0939 m2/g with the presence of water. Kerogen has more than 5 times SSA than shales', and does great contribution on gas adsorption for providing more SSA. Water reduces the SSA of shale and kerogen, because water molecules can simultaneously be adsorbed and condense in pores. Moreover, water decreases more SSA of shale than that of kerogen, because water can also decrease much more SSA of clay minerals in shale. The CH4 adsorption quantity of 300bar can be predicted based on HPMA data and Langmuir model. The predicted results indicate CH4

quality of dry N1 (Qdry=36 mg/g, Qwet=7mg/g) and N2 (Qdry=25mg/g, Qwet=6mg/g) kerogen decrease by 80% and 76% upon the wet kerogen created under 95% RH. Water in shale makes gas quantity of dry N1 (Qdry=7mg/g, Qwet=4mg/g) and N2 (Qdry=4.5mg/g, Qwet=3mg/g) shale reduced by 43% and 33%. Water reduce gas quantity of both shale and kerogen. Adsorption in kerogen is influenced more, since kerogen has bigger SSA. The contribution of kerogen adsorption in shale is estimated base on TOC (TOCN1= 4.9%, TOCN2=2.2%). Dry N1 and N2 kerogen can contributed 25.3% and 12.5% adsorption quantity for dry shale, which are quite bigger compared with the TOC. Wet kerogens contribute 8.6% and 4.5% adsorption quantity for wet shale. Results indicate kerogen does more contribution for shale gas adsorption under dry condition.Water decrease CH4 adsorption quantity in both kerogen and shale by taking up adsorption sites, blocking small pores and reducing the SSA. Gas adsorption in Kerogen is influenced more by water, reducing more than 70%. The stronger interaction between water molecular and the kerogen allowing water molecular competing adsorption sites with methane molecular. Gas adsorption in Kerogen contributes for shale, and dry kerogen can contribute more for shale adsorption than the wet one.