POROSITY EVOLUTION IN KEROGEN UPON THERMAL MATURATION: IMPLICATIONS FOR MAXIMUM LIQUIDS RECOVERY ZONE OF SHALE OIL

Yongge Sun, Peng Ni

Zhejiang University, Hangzhou 310027, P. R. China

The capacity of mudrock as economic reservoir is strongly dependent on their storage capacity, permeability and potential for fracture stimulation. The pores and pore network are extremely of importance to any assessment of shale reservoir quality. Also the ability to predict porosity trends along thermal maturation or buried gradients is a key issue in respect to sweet spot reservoirs, thereafter for successful well placement.

Organic matter-hosted pores, rather than mineral-hosted pores, are now considered to be the dominant contributors to total porosity and hydrocarbon storage in many organic rich unconventional reservoirs. The common working model of organic pore genesis holds that the abundance of OM-hosted is largely a function of thermal maturity. This means that porosity increases with thermal maturity. However, a linear relationship between OM-hosted porosity and thermal maturity is still not observed clearly, suggesting that the development and preservation of OM-hosted pore upon buried gradients are more complicated than expected.

Kerogen is the main component of OM in shale, and it is well known that methane and graphite are the ultimate products of kerogen thermal degradation with increasing temperature in deep earth. However, an evolitional trend to graphite strictly obeys a steady-state theory to zero free energy within reaction system and typically shows a dense-packing effect. Therefore, from a purely theoretical standpoint, OM-hosted pores should basically follow a bell shape accompanying hydrocarbon generation and expulsion, although secondary cracking of retained-bitumen in shale in the gas window could produce nano-pores as gas bubble. With this hypothesis, 43 shales from one lacustrine shale oil-producing section from the Gulf of Bohai Basin, North China, combined with one maturity sequence (6 samples) made by a high pressure, semi-closed thermal simulation system, were collected to investigate the porosity evolution in kerogen through oil window, using $N_2$ physisorption isotherms and swelling measurements. The main purpose is to probe the dynamics of the liquids storage capacity of kerogen through oil window, and make new insight on determination of maximum liquids recovery zone for shale oil exploration.

The semi-closed thermal simulation system was employed and its main advantage is that it can model the expulsion process accompanying hydrocarbon generation (Xie et al., 2015). Six experimental points were set at 300, 350, 400, 450, 500, and 550°C. The powered sample was heated from room temperature to a set-point, and then held isothermally for 72 hours under 80 MPa. The results demonstrate that oil window starts at 350°C (equivalent vitrinite reflectance of $\sim$0.8%$R_o$) and reach up to peak oil at $\sim$400°C (equivalent vitrinite reflectance of $\sim$1.1%$R_o$), followed by a maximum expulsion at 450°C (equivalent vitrinite reflectance of
Pore-size-distribution analyses show that average pore diameter in kerogen quickly increases accompanying oil generation, followed by a quick decrease after the maximum expulsion (Fig.1F). Field observation from lacustrine shale oil-producing section is totally agreement with this finding. As showed in Fig.1G-I, large amounts of oil generation start at the vitrinite reflectance of ~0.95%R₀, followed by occurrence of large amounts of hydrocarbon expulsion until to the vitrinite reflectance of ~1.15%R₀. The average pore diameter in kerogen shows the same trend as observed in the lab-simulated maturity sequence (Fig.1J). In addition, hydrocarbon storage of kerogen with increasing temperature demonstrates a sharp decrease to a stable level after the maximum expulsion, as revealed by swelling experiments with pentane and benzene as solvents. The FTIR and NMR measurements reveal that this could be induced by kerogen structure condensation (e.g. cyclization, aromatization, etc.) accompanying hydrocarbon generation and expulsion. It directly leads to a dense-packing effect except the sustaining preservation of pores in kerogen by mineral skeleton, suggesting that liquids storage capacity of kerogen strongly depends on oil expulsion from kerogen network, and the maximum liquids recovery zone in shale oil exploration could be defined in the range of vitrinite reflectance of ~0.9%R₀ to 1.2%R₀ in terms of OM-hosted pores as dominant contributors to hydrocarbon storage in many organic-rich unconventional reservoirs.

Figure 1 Hydrocarbon generation and expulsion with increasing temperature (A-F) and buried gradient (G-K), corresponding to the liquids storage of kerogen.

References