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Adsorption of mudstone source rock for shale oil – Experiments, model and a case study

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ABSTRACT

Inorganic minerals were separated from mudstone and shale to investigate their oil adsorption potential. A conceptual model was developed to reconstruct the oil adsorption capacity of underground mudrock/shale by combining adsorption and organic matter swelling data. The predictions for the free hydrocarbon oversaturation sorption zones in the Well NY1 profile were taken as a case study. The results suggest that the best depth for the shale oil prospect of the Es4s member strata lies between 3400 and 3600 m in the Dongying Depression. Hydrocarbon starvation zones occur mainly at a depth of < 3400 m, where both the maturity and the extent of oil conversion of organic matter are relatively low, while the sorption capacity of mudstone and shale rocks is by comparison high and the exploration risk is greater.

1. Introduction

The Dongying Depression, located in the middle of the Jiyang Super Depression in the Bohai Bay Basin, northern China, is a Meso-Cenozoic rift basin developed from the paleotopographical background of Paleozoic basement rocks. The main source rocks are the bottom section of the third member (Es3x) and the upper section of the fourth member (Es4s) of the Shahejie Formation (Fig. 1).

Shale oil shows have been observed in more than 300 wells in the Jiyang Super Depression, and industrial oil and gas flows, generally for a few days, were achieved in over 30 wells (Wang et al., 2013). In the Dongying Depression, shale oil was found in 12 wells, mainly within naturally fractured zones; two-thirds were discovered in the Es4s mudstone/shale stratum during conventional petroleum exploration, which differed greatly from the other depressions (Es1 and Es3 strata) of this basin. Recently, three vertical wellbores (FY1, NY1 and LY1) were drilled with water-based mud for shale oil. The goal of this study is to understand the shale adsorption potential. For mudstone or shale, oil adsorption on a whole rock is rarely conducted because of the high clay content and ease of slurry formation in solution, compared to sandstone reservoirs. Actual experimental study of the amount of oil absorption on shale minerals is needed. Based on experiments conducted on mineral fractions, we tried to evaluate the shale oil distribution in the Well NY1 profile through absorption measurements and modeling from organic geochemistry.

2. Experiments

2.1. Samples

Four mudstone/shale core samples were collected from the source rocks of the Shahejie Formation (Es3x and Es4s) in the Dongying Depression, Bohai Bay Basin (Fig. 1). One crude oil sample was produced from Well FY1, which is one of the three shale oil boreholes drilled with water-based mud. The essential characteristics of samples are listed in Table 1. The core samples were separated into minerals by immersion and flotation, and then these minerals and the oil sample were used to conduct the adsorption experiments.

2.2. Minerals separation

The mudstone/shale rock can be further divided into silica, calcium and clay minerals. The core samples were first cleaned and then submerged as whole rock in de-ionized water for about

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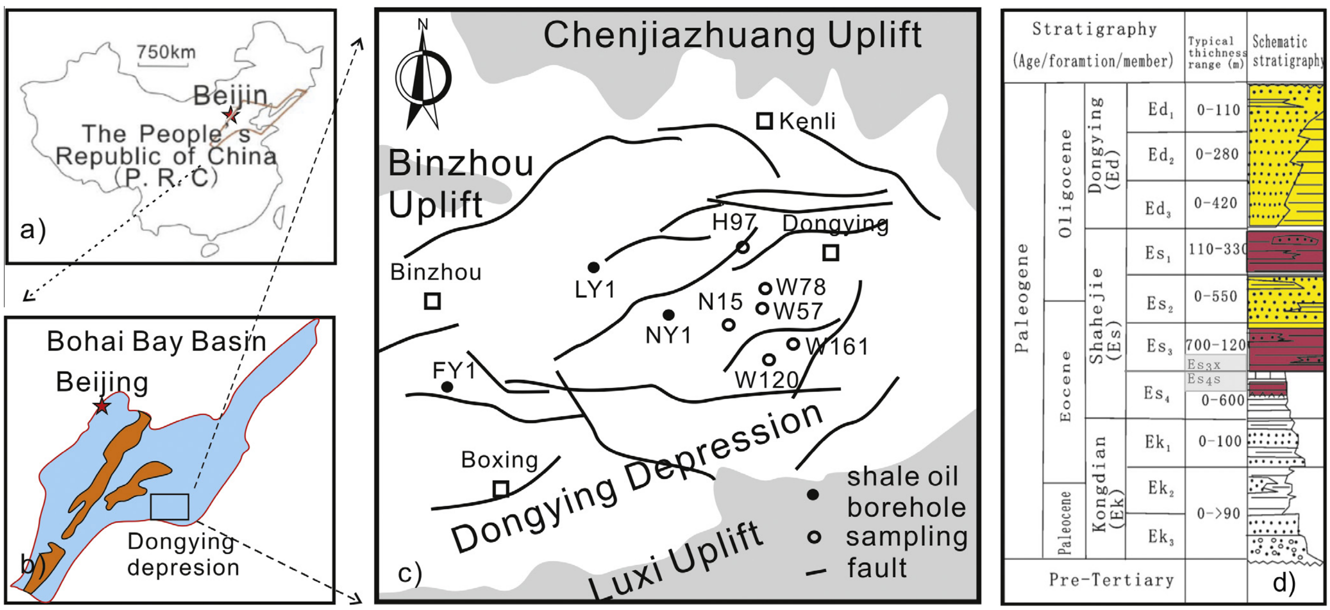

Fig. 1. (a and b) Location of the Dongying Depression, Bohai Bay Basin. (c) Distribution of sampling and shale-oil wellbores. (d) Tertiary stratigraphy of the Dongying Depression.

Table 1
Geochemical characteristics of mudstone and oil samples.

Well	Depth (m)	Stage	Sample	TOC (%)	S_1 (HC mg/g)	S_2 (HC mg/g)	S_3 (CO_2 mg/g)	T_{max} (°C)	HI	OI
W57	3419.0	Es3x	Mudstone	9.23	11.06	66.97	2.85	439	726	31
W78	3732.0	Es3x	Mudstone	2.40	4.98	9.53	1.73	439	397	72
He97	3182.5	Es3x	Shale	0.50	0.32	1.92	0.82	435	388	166
W161	1911.8	Es4s	Mudstone	3.89	1.27	27.78	3.78	430	714	97
FY1	3199	Es3x	Shale oil	Saturated (%)		Aromatic (%)	Resin (%)	Asphaltene (%)		
	–3210			61.5		18.0	14.0	6.5		

15 days until the samples are completely separated into independent grains. During this period, the samples submerged in the water were stirred gently 3 or 4 times daily to separate the minerals.

Thin carbonate laminae were observed in some shales, such as the sample He97. The sheet-like carbonate laminae were hand-picked when the samples were completely separated to produce so-called calcium pieces.

The fine grain clay minerals in the samples were obtained by the conventional settling method based on the Stokes formula (Pan et al., 2005). The water containing the clay minerals, which was held in a 2 L glass beaker, was allowed to settle for 20 min. Then, the top 10 cm clay-bearing water layer in the beaker was collected. The glass beaker was topped up with more de-ionized water and stirred again. After settling for 20 min, the top 10 cm clay-bearing water layer was again collected. This process was repeated seven times until most of the fine clay minerals were collected from the beaker. In this study, the amount of clay minerals collected was obviously less than that reported in previously published papers on the Dongying Depression (Li et al., 2010; Wu et al., 2013; Zhang et al., 2014). This may be due to the coarse, impure clay minerals as well as the clay agglomerate with organic matter (OM) not being collected in the lower water layer. The pure, fine clay minerals collected were suitable for the absorption experiment. The clay mineral compositions in the Shahejie Formation rocks are predominately a mixed-layer illite/smectite (72–92%), while kaolinite (4–12%) and pure illite (3–20%) are minor components (Lu et al., 1999; Pan et al., 2005; Zhang et al., 2006a,b; Li et al., 2010).

The quartz in the shale was separated and collected as follows. The samples containing the fine clay minerals and 'carbonate pieces' were separated and then dried at 80 °C. The dried samples were heated at 450 °C in a muffle furnace for four hours to remove the organic matter, and then treated with HCl to remove the carbonate. Finally, a heavy liquid $ZnCl_2$ solution (73%, liquid density ≈ 2.0) was used to remove the grains with a density less than 2.0. The residual silts were collected and taken as the 'quartz' fraction used to perform the absorption experiment. The XRD spectrograms of the mineral fractions and their composition are presented in Supplementary Data 1.

2.3. Oil adsorption on the minerals

The mineral fractions collected were extracted in a Soxhlet apparatus with dichloromethane for 48 h and then dried at 40 °C. The crude oil was diluted with toluene to the desired concentrations.

The experiments were carried out at constant mass ratio of mineral to crude oil solution (1:10) and initial concentrations of crude oil within the range 500–2000 ppm and the adsorbed amount was measured after 48 h equilibration at ambient temperature (about 25 °C). The initial oil concentration and the 48 h equilibration time were based on earlier experiments. Several spectroscopy methods have been used to detect the adsorbed amount by monitoring the variation in the solution concentration. The concentration of adsorbed asphaltenes or resins can be determined by UV spectrometry (Acevedo et al., 1995; Marczewski and Szymula, 2002); spectrophotometry (Pernyeszi et al., 1998;