Effect of clay and organic matter on nitrogen adsorption specific surface area and cation exchange capacity in shales (mudrocks)

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ABSTRACT

The resistivity log and its conventional application is one of the most important analysis used to find oil and gas saturated intervals. In unconventional oil and gas producing rocks, however, this tool and the consequent technique, is affected by many factors and not considered very reliable. Shale reservoir rocks usually have high total specific surface area (TSSA) due to high clay and total organic content (TOC) and nano-scale pores. Resistivity values are rather low and usually not indicative of reservoir zones in high TSSA rocks. Nitrogen adsorption and cation exchange capacity (CEC) are the common techniques to measure TSSA. Clays and organic matter (OM) affect the measured TSSA using either technique. This effect must be taken into account while calculating water saturation using conventional models. In this paper we investigate the mineralogical and geochemical associations of CEC and TSSA and their effects on resistivity in shale reservoirs.

We studied samples from oil and gas producing reservoirs such as Bakken, Haynesville, European Silurian, Niobrara, and Monterey formations. CEC was measured using Co(III)-hexamine^{3+} with the spectrophotometric technique and the equivalent TSSA (CEC-TSSA) was calculated. We also measured the specific surface area using sub-critical Nitrogen gas adsorption technique (N2-SSA). Rock mineralogy, organic matter properties and scanning electron microscope (SEM) images were used to further analyze the data.

We find that CEC values are directly correlated with the clay type and content regardless of the OM content or level of thermal maturity. Smectite and illite (when negligible smectite is present) dominate the CEC value in shales. N2-SSA correlates with clay content, especially smectite and illite, but is less sensitive to clay type as CEC. This correlation between N2-SSA and clay content was observed in Bakken (no organic matter), thermally mature (gas window) Haynesville, and low TOC (<2.67 wt%) Niobrara (oil window) samples. We also find that OM significantly affects N2-SSA in two different ways: (1) Blockage of pores and throats by bituminous kerogen, which limits the accessibility of nitrogen to clay surfaces. This effect was observed in thermally immature (oil window) Niobrara (TOC>2.6 wt%) and Monterey shales. (2) Development of nano-scale OM-hosted pores with high surface area mostly for thermally mature (gas window) shales as observed in high TOC (>1.5 wt%) Silurian shales. Correlation with N2-SSA and CEC values revealed that the average charge density for most of the shales in this study varies between 3 and 5 e/nm^2 and for some high TOC Niobrara samples can be as high as 32. Relatively higher charge density is due to underestimation of the TSSA by nitrogen adsorption technique. The correlation between SSA/CEC and clay content/type are well studied in the literature. However the results of this study aid in understanding how mineralogy, geological factors, organic matter content and thermal maturity affect this correlation in mud rocks from various reservoirs.

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1. Introduction

Presence of clays with high specific surface area (SSA) and its effect on resistivity log response has been investigated (for example, Archie, 1942; Waxman and Smits, 1968; Clavier et al., 1984; Revil et al., 1998). Unaccounted excess conductivity due to

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clay minerals results in underestimation of hydrocarbon volume in hydrocarbon producing reservoirs (Waxman and Smits, 1968). To evaluate the excess conductivity due to clay minerals, information is required about the number of counterions on clay surfaces, expressed as the cation exchange capacity (CEC) (Clavier et al., 1984). It was shown that the CEC and SSA are linearly correlated for clays (Woodruff and Revil, 2011) and shaly sands (Patchett, 1975; Revil et al., 2013). Therefore, accurate measurements of SSA and CEC as well as an understanding of their control factors are crucial for reliable resistivity log interpretation. The mineral or organic matter surfaces probed depend on the technique used for SSA measurement. For example, gas adsorption with inert gases (such as nitrogen) measures the external specific surface area (ESSA) (Derkowski and Bristow, 2012; Heister, 2014) whereas polar liquid (e.g. ethylene glycol monoethyl ether or EGME) adsorption techniques measure the total specific surface area (TSSA) (Heister, 2014; and Zhu et al., 2014).

Shales have high surface area because of high clay content (Passey et al., 2010) and nano-scale pores that are hosted by organic matter or minerals such as clays (Loucks et al., 2012; Milliken et al., 2013; Kuila et al., 2014). These rocks also have various amount of organic matter with different types and various levels of thermal maturity. Petrophysical and textural properties of the organic matter change as a result of maturation process (Zargari et al., 2013; and Zargari et al., 2015). Both clays and organic matter affect the measured CEC and surface area of shales in different ways. Clays, when present, dominate the measured CEC and SSA of the rock. There is a significant difference between the SSA and CEC of different clays (Table 1). Smectite and illite clays have the highest CEC and SSA and usually dominate the SSA of the clay rich rocks (Ellis, 1987; and Derkowski and Bristow, 2012). The effect of organic matter (OM), however, is more complicated than clay effect. OM can affect the SA measurements in three different ways: (1) Chemical interaction with the investigating fluid that is used for SSA or CEC measurement (Chiou et al., 1993; Derkowski and Bristow, 2012), (2) it can Limit the accessibility of the investigating fluid to the surface of the minerals by blocking the pores and throats or coating the clay surfaces themselves (Lang and Kaupenjohann, 2003; Mikutta et al., 2004), (3) Developing nano-scale pores as a result of thermal maturation and diagenesis of the organic matter (Kuila et al., 2014; and Zargari et al., 2015). Chemical interaction and developing nano-scale pores might

increase the measured CEC and SSA, whereas, the blockage of the pore space and coating of the clay surfaces decrease the measured SSA.

The effects of clay and OM on CEC and SSA are well studied in soils (Chiou et al., 1993; Peinemann et al., 1999; Maček et al., 2013; and Heister, 2014). However, the interactions between OM and clays and their effects on the CEC and SSA in organic-rich sedimentary rocks are largely unknown and more complicated due to diagenetic changes in OM and mineral properties. Controversial results are reported especially on the effect of OM on CEC and SSA. Zhu et al. (2014) report positive and negative correlations between TOC with various textures and morphologies and SSA measured by N2 and EGME techniques for oil bearing mudrocks from eastern China. In this study, the overestimation of TSSA with the EGME method in presence of OM is neglected Derkowski and Bristow (2012); Keil et al. (1994) and Mayer and Xing (2001) report an increase in TSSA (measured by retention techniques) with increasing OM content in immature and non-altered soils. A similar correlation is reported for black shales from Late Cretaceous black shales of the Deep Ivorian Basin by Kennedy and Wagner (2011) and Kennedy et al. (2002). However, a negative correlation between TOC and SSA was observed by Kuila et al. (2012) for oil window Niobrara samples and by Ding et al. (2013) for muddy source rock and oil shale from the Oligocene Shahejie Formation.

Our literature survey revealed that several factors need to be considered during comparisons of results from different studies or formations: (1) the technique that is used for SSA or CEC measurement and their advantages and limitations, (2) TOC and level of thermal maturity, (3) clay type and content and (4) organic matter texture and distribution. A comprehensive study of the effect of rock composition and organic matter on CEC and SSA for shales considering all these factors is lacking.

In this study we present CEC and SSA data for rock samples from different oil and gas producing shales. We cover a wide range of clay content and type, TOC and thermal maturity and organic matter texture to study the effect of rock composition on the measured CEC and SSA. We also compare the SSA calculated from CEC data and measured by nitrogen adsorption technique (N2-SSA) and provide insights on application of these values for resistivity log interpretation.

2. Materials

In this section we briefly describe the dominant mineralogy, thermal maturity, organic matter type, and organic matter content for the samples used for this study (Fig. 1). The details of each sample set have been presented by Kuila (2013) and Saidian et al. (2016) (Haynesville, Niobrara, and Eastern European Silurian), Rivera et al., 2014 and Godinez, 2013 (Monterey), and Saidian and Prasad, 2015 (Bakken). The key properties of kerogen and clay for all sample sets are given in Table 2.

2.1. Bakken

Samples from Middle Bakken and Three Forks formations were carbonate rich, mainly dolomite with moderate amount of clay and quartzo-feldespic. The clay was mainly illite and no organic content was present (Fig. 1a).

2.2. Haynesville

Haynesville samples were clay-rich with moderate amounts of quartzo-feldspathic constituents and carbonate (Fig. 1b).

Table 1
Cation exchange capacity (CEC), nitrogen adsorption specific surface area (N2-SSA) and ethylene glycol monoethyl ether total specific surface area (EGME-TSSA) for different clay types and isolated kerogen.

Sample	CEC (meq/100gr)	SSA-N2 (m²/gr)	TSSA-EGME (m²/gr)
Smectite[a]	76.1–150[b–f]	31.13[i], 75.9[j]	400–850[h,m]
Illite	9–40[b–d,f,g]	25[k], 67.2[j]	57–118[h,m]
Chlorite	1[c]	15[k]	9–62[h,m]
Kaolinite	0.9–15[a–e,h]	11.5[i]–21[j]	9–62[h,m]
Kerogen	<0.5[h]	5.5–300[l]	860–921[h]

[a] Smectite and different types of Montmorillonite are combined.
[b] Wiklander (1964).
[c] Thomas (1976).
[d] Ridge (1983).
[e] Ellis (1987).
[f] Blum and Eberl (2004).
[g] Środoń (2009).
[h] Derkowski and Bristow (2012).
[i] Kuila and Prasad (2013).
[j] Chiou et al. (1993).
[k] Van Olphen and Fripiat (1979).
[l] Cao et al. (2015).
[m] Revil et al. (2013).