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Geochemical Properties of Shale Gas Reservoirs and Their Impacts On Gas Development: A Review

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ABSTRACT: Unconventional shale gas resources have rapidly gained global importance and increase over the past few years and are predicted to contribute up to 26% of the global energy resources by the year 2035. These unconventional reservoirs are very heterogeneous and complex in terms of their geological, geochemical, petrophysical, and geomechanical properties. These complexities create many challenges during their exploration and production, especially, in the screening of exploration targets, drilling of horizontal wells and identification of intervals for fracturing, fracturing fluid composition and impact of produced water and flow-backs on the environment, and prediction of gas production rates and estimated ultimate recoveries. It is difficult to develop a general model for shale gas because: 1) there are many variables that influence gas transport and storage capacity in shale reservoirs, and 2) no two shale gas reservoir rocks are the same. Therefore, optimization of gas production from shale gas reservoirs depends upon a detailed knowledge and fully integrated analysis of the reservoir properties. This study provides an insight into the geochemical properties of shale gas reservoirs that are key to the efficient characterization, exploration, gas flow and transport mechanisms, and the economic production of natural gas from these complex reservoirs.

KEYWORDS: Shale gas reservoir; organic matter, thermal maturity; mineralogy; gas adsorption; organic micropores.

I. INTRODUCTION

Unconventional shale gas resources have rapidly gained global importance and increase over the past few years and are predicted to contribute up to 26% of the global energy resources by the year 2035. Shale gas discovery, exploration and development in many countries (about 41 countries) have changed the global energy supply structure. These unconventional reservoirs are characterized by high heterogeneities and complex behavior, which are functions of their petro-geological, geochemical, petro-physicals, geomechanical and mineralogical properties. Geological characteristics of shale gas formations influence their geomechanical properties and thus horizontal well drilling and fracturing designs. Geochemical properties are highly responsible for the desired shale beds, particularly organic richness, maturity, and thickness. Petrophysical properties play a major role in the exploration and development of shale gas reservoirs. Petrophysical characterization is an important step towards an improved understanding of the geology of a shale formation. It is the starting point towards successful hydraulic fracturing of the shale rock and provides vital data for wells location and gas production design and optimization (Killough et al. 2013). Adequate knowledge of the geochemical and petrophysical properties is very essential for shale gas resources evaluation. Geomechanical properties are required to understand strength and stiffness of shale rocks, whether they will be brittle enough to initiate fractures within and keep such fractures open or whether they will be ductile, and allow fracture self-healing. This is very vital for exploration and successful production of gas from the reservoir. Geomechanical properties are fundamental to drilling, fracturing and gas production. Geomechanical and rock mineralogical properties are related. The mineralogical characterization of shale rocks has a significant effect on the efficiency of shale gas, especially for drilling and production operations (Shoieb et al. 2017). The mineralogy of shale gas reservoirs accounts for the potential of shale rock to source and store hydrocarbons. The presence and abundance of quartz and swelling clay minerals and trace elements, including NORM, not only indicate the potential of a shale rock as an economic gas resource, but also provides important information for well drilling planning and produced water management. This is because these minerals are sensitive to drilling fluids and drilling techniques, and harmful to the environment. These minerals and trace elements are needed for the assessment of the potential for environmental impacts during hydraulic fracturing.

Shale gas resource plays are currently undergoing active exploration and development stages in hydrocarbon production globally. However, despite the experience gained so far and the intense activities witnessed in shale gas development, understanding the science, engineering and technological controls on reservoir quality and successfully exploitation of shale gas formations has remained a great challenge. Therefore, an adequate understanding of shale geochemistry, geophysics, geomechanics and mineralogy of a shale gas rock is very important in understanding the potential of the shale as a hydrocarbon reservoir and its ability to yield gas in commercial quantity when fractured. This study focuses on the geochemical properties that characterize shale gas reservoirs.

II. GEOCHEMISTRY OF GAS SHALES

Unconventional shale gas reservoir is a naturally self-sourced, self-stored, and self-sealed mineral system gathered in the dark, very fine grained rocks known as mudrocks or mudstones with typically fine grain-sized sedimentary rock made up of silt ranging from 4 μm to 62.5 μm (0.004-0.0625 mm) and clay size particles less than 4 μm (<0.004 mm) in size (Merriman et al. 2003; Passey et al. 2010). These tiny grains are generally made up of a mixture of clay minerals such as quartz, feldspar, mica, chert, as well as other clay-size mineral particles (smectite, illite, kaolinite). Other constituents might include, in varying quantities, organic particles, carbonate minerals, iron oxides, sulfide minerals (pyrite) and heavy mineral grains. The type and quantity of these other constituents in the rock are largely dependent on the environment of deposition of the shale, and are often responsible for the color of the rock. For example, iron oxides are responsible for red or yellowish coloring while carbonaceous compounds and pyrite impart black coloring to the grains (Cao et al. 2017). Hydrocarbon components in shale gas are mainly methane (CH_4), ethane (C_2H_6), and hydrocarbons heavier than ethane (C_3+). Common non-hydrocarbon gases are mainly hydrogen (H_2), nitrogen (N_2), carbon dioxide (CO_2), hydrogen sulfide (H_2S), as well as rare gases such as helium (He) and argon (Ar) (Zhao et al. 2013).

Knowledge about the variable lithologies, mineralogies, and organic matter content is vital for identifying favorable intervals for gas production and for improving well placements and hydraulic fracturing design and strategies. Important geochemical properties that characterize shale gas reservoirs, and that are used in evaluating the hydrocarbons generation potential of a shale rock include organic richness (total organic carbon (TOC), quality of organic matter type (I-V), kerogen content (visual kerogen, hydrogen index – HI, and oxygen index - OI), thermal maturity level (vitrinite reflectance - T_{max}), and rock mineralogy (Josh et al. 2012; Jarvie and Rezaee 2015; Peters et al. 2016).

Comprehensive analysis of the properties in over-mature shales (Marcellus, Longmaxi, and Qiongzhusi) and their effects on shale gas carried out by Zhang et al. (2018) shows that (a) organic matter formed a material basis for shale gas generation, (b) porosity provided the capacity for shale gas accumulation, and (c) moderately high thermal maturity (Ro up to 3%) improved the storage space through elevating porosity. This indicates that total organic carbon, porosity, and thermal maturity in over-mature shales are the main factors affecting shale gas accumulation. Therefore, an understanding of the relationship between the geochemical properties and the petrophysical properties (pore matrix, porosity, and permeability) of a shale gas reservoir is fundamental to the evaluation of the complex multiphase behavior and the mechanisms of gas diffusion, transport and gas recovery, and the environmental impact of produced water. These geochemical properties are treated in the subsections that follow.

Organic richness : Gas in shale reservoirs are sourced from sedimentary organic matter (OM). The presence, type, quantity, and quality of organic matter in a shale reservoir depend on the biological origins of the organic matter and setting of the original environment of deposition. Environment of deposition may be marine or non-marine, shallow marine or deep marine, oxic (aerobic) or anoxic (anaerobic) (Demaison and Moore 1980). The relative quantity and quality of organic matter preserved from the deposited biomass is a key parameter that determines the overall volume of gas that can be generated from the deposited biomass. The concentration and composition of organic matter preserved during deposition and diagenesis of sediment ultimately determines the hydrocarbon generative capacity of the rock. In general, many parameters are considered in the evaluation of shale gas reservoirs. These include organic matter (richness, type and maturity), mineral composition in shale and environment and conditions of accumulation. The typical shale is rich in organic matter content, with the total organic carbon (TOC) content in the range of 1%–20% (Zhang et al. 2017).

Total organic carbon : Total organic carbon (TOC) is a measure of the dry weight per cent of organic carbon within hydrocarbon source rocks. Natural gas (mainly methane, ethane and propane), are usually, but not always, generated by the action of heat on organic carbon due to burial over geological time. Carbon is contained in all organic components of a rock, namely, kerogen, bitumen and hydrocarbons (Steiner et al. 2016). TOC is a critical geochemical parameter for quantitative characterization of shale gas reservoir rock and is an indicator of organic richness. Total organic carbon is used to evaluate the hydrocarbon generation potential of source rocks in shale gas reservoirs. The TOC content, together with the thickness of organic shale and organic

maturity, are key attributes that are essential in evaluating the economic viability of a shale gas play. Estimation of total organic carbon (TOC) is therefore a major task of geochemical characterization of shale gas formations
It is said that excellent shale gas reservoirs are determined by a combination of high TOC values and high quartz concentrations. High TOC values more than 2% indicate that the unit has excellent potential as a source rock (i.e., more gas production in situ). It has been reported that rocks containing less than 0.5% TOC are considered as poor source rocks. Between 0.5 and 1% TOC value indicates fair source rock. TOC% value between 1 and 2% indicates good source rocks and TOC value between 2% and 4% indicate very good source rocks. TOC% values above 4% often indicate highly reducing environment with excellent source potential (Peters and Cassa 1994; Ross and Bustin 2009). The abundance of quartz grains within these fine-grained reservoirs makes the rock brittle and more prone to failure, increasing the effectiveness of reservoir fracturing techniques, and therefore increasing the production of gas. In the presence of moisture clay-filled minerals tend to hydrate and fill and close fractures, causing significant reduction in porosity and permeability of the reservoir, which in turn affect drilling, hydraulic fracturing and gas production.

Shale rock with more than 2% total organic content (TOC) often has significant source potential. When TOC is between 1 and 2%, depositional environment intermediates between oxidizing and reducing, and TOC above 2% indicates reducing environment with excellent potential for hydrocarbon generation (Demaison and Moore 1980; Bissada 1982; Leckie and Kalkreuth 1988; Bacon et al. 2000; Salleh et al. 2008; Boruah and Ganapathi 2015; El Nady et al. 2015).

There is however, no unique combination or minimum amount of these factors that determines economic viability. The factors are highly variable between different shale formations and can vary, in fact, within a single deposit or stratum of shale over short distances. At the low end of these factors, there is very little gas generated. At higher values, more gas is generated and stored in the shale (if it has not been expelled from the source rock), and the shale can be a target for exploration and production. For example, a study of shale gas plays in the United States reveals a variety of geochemical and geological parameters unique to each play. The primary point here is that the geochemical characteristics of each shale gas deposit are relatively unique and must be carefully examined to determine resources. However, properties like maturation of the organic matter and hydrocarbon type influence TOC measured on both core plugs and well logs. TOC in a gas-bearing source rock play mostly denotes carbon associated with kerogen as carbon density of gas is generally too low to be detectable. Total organic carbon is a mix of kerogen, bitumen and liquid hydrocarbon. It is a critical parameter for determination of reservoir quality of a source rock and is present in all organic components of a rock, namely, kerogen, bitumen and hydrocarbons (Salleh et al. 2008; Zhang et al. 2018).

Organic matter type : The organic matter type is a key parameter in evaluating gas source rock potential and is an important factor influencing the development of organic pores and the nature of the hydrocarbon products (Loucks and Reed 2014). Organic matter type influences the development of organic pores in shales (Loucks and Reed 2014; Nie et al. 2018; Tang et al. 2018). The organic matter Type I has very good hydrocarbon generation potential to develop massive organic pores. In the case of shale maturity, there are few or no pores within the kerogen (Loucks et al. 2009). Organic pores are formed within the kerogen as the solid kerogen undergoes thermal transformation and hydrocarbon generation (Ross and Bustin 2007; Reed and Loucks 2007; Loucks et al. 2009; Bernard et al. 2012; Lohr et al. 2015). Organic pores start developing after shale maturity reaches a threshold of 0.75% R_O (Er et al. 2016). Analysis of the relationships between pore geometry and mineral components and between TOC and maturity of organic matter indicates that depositional environment, diagenesis, and thermal evolution of organic matter control the formation and preservation of pores (Er et al. 2016). In addition, hydrocarbon is adsorbed on the surface of the organic matter, which could have caused the expansion of kerogen and then the reduction of organic pore. Difference in physiochemical structure of organic matter played an important role in formation and evolution of organic pores (Ma et al. 2017).

Kerogen : Kerogen is a high molecular weight carbonaceous organic matter (OM) from the condensation of organic residues in sedimentary rocks, and serves as source material for the oil and gas in shales (Agrawal et al. 2017; Weck et al. 2017). Kerogen (together with bitumen) is formed when deposited organic matter is diagenetically altered by heat and pressure of burial (Vandenbroucke 2003; Wolchover 2011; Atmani et al. 2017).). Kerogen is not soluble in organic solvents and has a low bulk density (1.3 gm/cc), very high gamma ray linked with uranium, low photoelectric factor (about 0.24 barns/electron), and high neutron porosity (about 60 p.u.). When kerogen is subjected to increased temperature and pressure with increasing burial depth, it undergoes catagenesis and is converted into oil and gas. Therefore, measurements of source rock thermal maturity are important for understanding the quantity, quality, and timing of generation of petroleum that may have been produced by a particular source rock. In addition to its carbon skeleton, kerogen is also predominantly made of hydrogen and oxygen, as well as residual nitrogen and sulfur (Weck et al. 2017). The hydrogen content of immature kerogen is a key indicator of kerogen type and, because hydrogen content decreases with thermal maturation, it can also be used to assess relative thermal maturity. Both the hydrogen content and thermal maturity are critical in assessing the petroleum charge in a sedimentary basin. Petroleum-generating systems with high hydrogen-to-carbon (H/C, > ∼1.2) elemental ratios tend to generate more oil during catagenesis than kerogens with lower H/C ratios

Kerogen type : Chemically, the major kerogen types in shale gas source rocks include Type I, II, III, IV (Harwood 1977; Mroczkowska-Szerszeń et al. 2015; Haris et al. 2017). The types of **kerogens** present in a rock largely control the type of hydrocarbons generated in that rock. Different types of kerogen contain different amounts of hydrogen relative to carbon and oxygen. The hydrogen content of kerogen is the controlling factor for oil/gas yields from the primary hydrocarbon-generating processes. Kerogen type I is abundantly rich in hydrogen and therefore is oil prone; type II is moderately rich in hydrgen and therefore oil and gas prone; type III is gas prone as it contains small amount of hydrogen; type IV is not prone to either oil or gas (primarily composed of vitrinite) or inert material, does not contain hydrogen and is therefore of no much interest to petroleum geologists in terms of shale gas resources. It may however, be more prone to generate coal (McCarthy et al. 2011). A mixture of kerogen types II and III is predominantly deposited in the shallow and restricted marine environment under prevailing reducing conditions and is prone to oil and oil/gas production (El Nady and Hammad 2015). Kerogen type and maturity determine the oil/gas ratio, and volume establishes whether there is sufficient economic potential to continue gas production.

Kerogen type is defined according to hydrogen-carbon ratio (H/C) and oxygen–carbon ratio (O/C) or hydrogen index (HI) and oxygen index (OI) values and Rock-Eval hydrocarbon pyrolysis yields (S2). The most useful of these parameters is thought to be the hydrogen index (HI), which is the mass ratio of thermally pyrolyzable kerogen (S2) to the total organic carbon (TOC) content in a sample (HI = 100 × S2/ TOC, milligrams of hydrocarbons per gram of TOC) (Meehan 2010). The HI is a proxy for the hydrogen content and is a stand-in for the kerogen H/C ratio, i.e., HI is only an indicator of the hydrogen content of a sample and not a direct measurement of the organic hydrogen and does not always correlate well with H/C ratios. Waples (1985) used the hydrogen index values (HI) to differentiate between the types of organic matter. He showed that kerogen with high pyrolysis yields (S2) (>15 mg HC/g rock), (hydrogen indices above 600 mg/g), usually consists of type I or type II kerogen and has excellent potential to generate oil, kerogen with hydrogen indices between 300 and 600 mg/g contains a substantial amount of type II macerals and is considered to have good potential for generating oil and minor gas, while, kerogen with low pyrolysis yields (S2) (10 < 15 mg HC/g rock), (HI 150 and 300 mg/g) contains a mixture of types II and III kerogen, with type III more than type II and therefore is capable of generating mixed gas and oil but mainly gas. Kerogen with low pyrolysis yields (S2) (<10 mg HC/g rock), (HI below 150 mg/g) indicate a potential source for generating gas and is mainly type III kerogen.

One of the basic methods for chemical characterization of organic matter in shale is the elemental analysis of its carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulphur (S) contents (Taylor et al. 1998; Mark et al. 2007; Gazulla et al. 2012). Rock-Eval pyrolysis is widely applied for faster, easier, and preliminary screening of sedimentary rock in order to determine the type, quantity, thermal maturity and hydrocarbon potential of organic material. However, it has been stated that the Rock-Eval or Source-Rock-Analyzer (SRA) data (i.e. HI, OI and S2) does not always accurately represent the types of kerogen present and the types of hydrocarbon that may be generated by the source rocks. This is because mineral matrix within the source rock influences Rock-Eval kerogen/SRA typing result. In addition, sediments with TOC contents of less than 2.0% can result in a significant reduction in HI. Thermal decomposition of carbonate minerals during the Rock-Eval analysis/SRA contributes carbon dioxide and increases the oxygenation index (OI) in low TOC sediments (Baskin 1997).

Thermal maturity : Thermal maturity defines the degree of thermal or diagenetic transformations that occur in the organic matter contained in hydrocarbon source rocks which generate hydrocarbons– from the immature phase through the main phase of oil and gas generation to the post-maturity phase. These transformations are driven by temperature, pressure, and time, environment of deposition, and minerals or substances which catalyze or inhibit chemical reactions resulting from burial of the organic matter. The degree of thermal maturity depends primarily on temperature and on the time of exposure to that temperature. Of all these parameters, temperature is the most important factor controlling hydrocarbons generation. Temperature increases with increasing overburden, causing the carbon-carbon bonds of the organic molecules in the organic matter to rupture. Maturity increases with burial depth due to higher temperatures that prevail in deeper parts of the rock (Grotek and Janas 2014a). The effect of pressure on thermal maturity of organic matter is minor, as pressure reduces the rate of chemical reactions that are involved in maturation processes because of the increase in volume of liquids involved in the formation of hydrocarbons. Under high pressure in a closed rock system the rates of reactions become slower, leading to reduction in gas generation. Pressure controls organic matter maturation by retarding initial increase in viitrinite reflectance gained during heat-up. In addition to temperature, pressure affects the subsequent rate of formation of viitrinite reflectance and must be considered in the formulation of rate equation to describe its evolution, activation time and viitrinite reflectance gained during heat-up (Bayon 2012)

Measurement of vitrinite reflectance is widely used for determining maturity of organic matter in shales. Vitrinite is a shiny material formed by the thermal alteration of organic matter. It is present in most kerogens and is often be used, in conjunction with TOC values, pyrolysis data, etc. to describe the maturity of organic matter in shales. Vitrinite reflectance increases with increasing time and temperature in a predictable manner in relation to the generation history of organic sediments. It is usually measured and defined in terms of reflectance in oil, Ro as reference standards. While Ro is a measure of thermal maturity, it is basically a function of the type of kerogen being evaluated. At Ro less than 0.5% the shale cannot generate much oil and is therefore categorized as thermally immature. Shale with Ro of 0.9–1.0% has been baked by temperatures leading to maximum oil generation. Ro of 1.3% represents the upper limit for oil generation, above which the shale will only produce condensate (light oils) or gas. This degree of thermal alteration called the gas window occurs at temperatures of 120 – 150ºC and is expressed by reflectance index values of 2 - 2.0% Ro. The alteration processes will continue until the source rock becomes overmature and its hydrocarbon generative potential is exhausted (>3.0% Ro) (Grotek and Janas 2014b). At high thermal maturity (>4% R_o), the conversion of organic matter to graphite-like carbon (turbostratic carbon) occurs (Rudnick 2016).

Thermal maturity is the primary factor that determines whether a source rock can produce oil, gas or condensate (Lecompte et al. 2010; Yang et al. 2017). It is a key parameter for the determination of potentially prospective shale oil and gas accumulations at initial stages of exploration. Based on thermal maturity values, source rocks are categorized as thermally immature, mature or post-mature rocks in terms of capability to generate hydrocarbons. Also, according to Grotek and Janas (2014b), thermally immature or unaltered source rocks, at relatively small depths, may generate (biogenic) natural gas which is formed by certain bacteria species as a result of their metabolic activity at temperatures below 50ºC. For such rocks the degree of organic matter alteration, as expressed by reflectance index not more than 0.5% Ro. As the source rock is buried, overburden increases and bacterial organic matter alteration subside, while temperatures and pressures of the rock increase and gradually trigger chemical changes that lead to the generation of oil and smaller quantities of natural gas. A rock which had been heated so as to generate crude oil is called mature rock in the oil generation phase or oil window, and its degree of alteration, expressed as vitrinite reflectance index, Ro, ranges from 0.5 to 1.2% Ro. At greater depths, the source rock will generate mostly thermogenic natural gas. Accordingly, a mix of the previously generated oil and the newly generated gas (condensate) is expected to occur in the rock. If the rock medium is deeper buried, organic matter will generate thermogenic natural gas only. Any oil previously accumulated in the rock will be transformed into thermogenic natural gas. This degree of thermal alteration called the gas window occurs at temperatures in the order of 120 – 150ºC and is expressed by reflectance index between 1.20- 2.0% Ro. The process will continue until alteration processes reach the degree at which the source rock becomes over-mature and its hydrocarbon generative potential is exhausted (>3.0% Ro). This occurs at temperatures in excess of 200ºC.

III. SHALE MINERALOGY AND GEOCHEMISTRY

Shale and mudstones consist of diverse types of major and trace elements among which are quartz (silica), clay minerals, carbonate minerals (calcite, dolomite), feldspars, mica, pyrite, phosphates, and others, in negligible quantities (Zhang et al. 2017). Trends in the values of these minerals are useful indicators for accessing potential source and reservoir rocks. For example, the proportion of the two major mineral phases silica and carbonate, as well as their types of occurrence, provide an understanding of depositional environment, water geochemistry, organic richness, maturity and reservoir petrophysical properties (Hosseininejad et al. 2012; Chermak and Schreiber 2014). It is therefore very crucial to understand the mineral composition and geochemical characteristics for a proper evaluation of shale gas rocks. This is necessary for creating proxies of depositional environment, chemistry of water, provenance and diagenetic changes during and after deposition, resulting in different hydrocarbon-source and reservoir properties.

The presence of minerals in shale has major effects on the physical properties of shale gas reservoir (Diaz et al. 2013; Al-Ismail and Zoback 2016). First, high content of brittle minerals easily leads to natural fractures and stress-induced fractures (Ding et al. 2012; Wang et al. 2013; Chopra et al. 2014; Yasin et al. 2017), while in artificial or hydraulic fracturing, high content of brittle minerals cause the formation and extension of fractures. An example is Barnett shale which is able to produce large volume of gas due to its brittleness and response to artificially-induced fractures (Altamar and Marfurt 2014; Zhang et al. 2015). Second, apart from organic matter, clay minerals in shale rock exhibit large capacity to adsorb gas. Gas adsorption capacity increases with increasing clay mineral content in shale (Ross and Bustin 2008; Zhang et al. 2013; Zhong et al. 2016). However, increased clay mineral particles easily block gas seepage path, thereby significantly reducing the matrix permeability (Ghanizadeh et al. 2013; Wang et al. 2014; Cao et al. 2016). On the other hand, high quartz content increases the permeability significantly, thereby countering the impact of increased clay content in the reservoir (Heller et al. 2014; Watanabe et al. 2017). Shale gas reservoirs with high siliceous and carbonate mineral contents have very high brittleness resulting to the rock being prone to form natural and induced fractures for gas seepage under the action of external force (Ding et al. 2012; Wang et al. 2013; Dan et al. 2016). Therefore, increase in carbonate minerals content would block mudstone-shale pores, which will result in the decrease of porosity. On the whole, carbonates have inhibitory effect on development of pores and fractures (Nie and Zhang 2011; Luo et al. 2013; Cao et al. 2015; Huang and Shen 2015; Lee and Kim 2016).

The mineralogical characterization of shale rocks has a significant effect on the efficiency of shale gas, especially for drilling and production operations. Mineralogical analysis associated with microscopic work provides sufficient knowledge to understand the type and abundance of mineralogical phases present as a key factor in evaluation of the hydrocarbon potential of shale. An understanding of shale geochemistry and mineralogy is very important to understanding the potential of shale rock to generate, store and produce natural gas when stimulated.

IV. SHALE GAS DESORPTION

Gas desorption is essential to understanding the production capacity of a shale gas reservoir (Passey 2010; Yang, et al. 2015; Wang et al. 2016; Tang et al. 2017). This is because, the shale can hold significant quantity of gas adsorbed on the surface of organic matter, including clay minerals (Mengal and Wattenbarger 2011; Guo et al. 2015). In shale, methane molecules are mainly on the carbon-rich components, eg kerogen, which is usually quantified in terms of total organic carbon (TOC). Thus, significant amount of natural gas can be produced from the surface of kerogen (Guo et al. 2014).

Organic matter is the key element that controls gas adsorption in shales. Total organic carbon (TOC) value has a significant impact on gas adsorption capacity in shales. It has been shown that high pressure methane isotherms on dried and moisture equilibrated shales indicate a general increase of gas sorption with increase in total organic carbon (TOC) content (Ross and Bustin 2009). Thus, gas adsorption capacity depends on TOC, organic matter type, thermal maturity and clay minerals. The higher the TOC content the greater the gas adsorption capacity (Yan et al. 2013; Zhao et al. 2014). This is because organic carbon is characterized by a lot of micropores. Micropore types and microporosity increase with TOC. Thus, TOC also has certain influences on free gas (Nie and Zhang 2012). Organic-matter type and thermal maturity affect gas sorption rate but the presence of moisture can greatly reduce gas sorption capacity (Zhang et al. 2012; Zhang et al. 2013). During different thermal evolution stages, certain processes such as: hydrocarbon-generation mechanism, development of organic matter pores, and methane storage/transport mechanism in organic matter/pores basically affect shale gas desorption and production (Yu and Sepehrnoori 2014; Mehrabi et al. 2017; Miao et al. 2018).
Zhang et al. (2013) conducted a series of CH_4 adsorption experiments on natural organic-rich shales, isolated kerogen, clay-rich rocks, and artificially matured Woodford Shale samples under dry conditions. Their results indicate that physic-sorption is a dominant process for CH_4 sorption, both on organic-rich shales and clay minerals. They stated that methane sorption capacity increases with increasing thermal maturity due to the presence of nanopores produced during organic matter decomposition. Furthermore, CH_4 sorption on clay minerals is mainly controlled by the type of clay mineral present. In terms of relative CH_4 sorption capacity: montmorillonite ≫ illite – smectite mixed layer > kaolinite > chlorite > illite (Ding et al. 2016).According to Zhang et al. (2013), the effect of rock properties (organic matter content, type, maturity, and clay minerals) on CH_4 adsorption can be quantified with the heat of adsorption, q, which ranges from 9.4 to 16.6 kJ/mol., and the standard entropy, determined from adsorption isotherms at different temperatures. These values are considerably smaller than those for CH_4 adsorption on kerogen (21.9–28 kJ/mol) and organic-rich shales (15.1–18.4 kJ/mol). The affinity of CH_4 molecules for sorption on organic matter is stronger than for most common clay minerals. Thus, it is expected that CH_4 molecules may preferentially occupy surface sites on organic matter. However,

active sites on clay mineral surfaces are easily blocked by moisture. As a consequence, organic-rich shales possess a larger CH_4-sorption capacity than clay-rich rocks lacking organic matter. It is critical to understand the multistage gas desorption process in order to adequately analyze shale gas transport phenomena and reservoir flow capacity necessary for designing production scheme for sustained economic gas recovery. Knowledge of gas transport process in shale matrix is of great importance in designing development strategies and in formulating appropriate predictive mathematical models for the complex multiphase behavior of shale systems (Wopara, 2018). Knowing the contribution of each gas source to gas transport history and to ultimate gas recovery is of great importance to the design and management of shale gas development projects.

V. CONCLUSION

This study has looked at the geochemical properties of a shale gas reservoir that characterize its potential to generate, reserve, and yield gas when fractured. Such geochemical properties as organic richness, total organic carbon, organic matter type, thermal maturity, shale mineralogy and high brittleness, fractability, and good gas adsorption/desorption capability are the hallmarks of an economic shale resource. Geochemistry is a powerful tool for the analysis of shale gas reservoirs. Geochemical properties play a major role in the characterization and successful development of shale gas reservoirs. No two shale gas reservoirs are the same and each layer or interval facies in a given reservoir is different from the others in terms of geochemical properties, minerals composition, and petrophysical characteristics. Therefore, the geochemical characteristics of individual shale gas reservoir must be specifically examined to determine its potential to generate gas, and its capacity to store and transport the gas so generated. Understanding geochemistry and mineralogy is very critical in mitigating the risks inherent in shale gas resource evaluation, development, and management. Knowledge of shale geochemical properties such as organic richness, hydrocarbon source potential, thermal maturity, environment of deposition, depth of burial, quantity of absorbed gas, volume of gas in place, type of minerals, etc., is very critical to understanding the capability of a shale rock to generate and retain gas, resources evaluation and development strategy, and of strategies for increased well drilling, completion, design of hydraulic fracturing, and gas production efficiency from these complex reservoirs.

Reservoir quality (RQ) and completion quality (CQ), two shale gas well performance indicators, depend to a large extent, on shale mineralogy. Reservoir quality (RQ) indicator include effective porosity, total organic carbon (TOC) content, matrix permeability, hydrocarbon saturation, while CQ indicator include minimum fracture closure stress, brittleness index (BI). These parameters when matched, give an indication of the impact of shale mineralogy on RQ and CQ in a given shale gas reservoir. Geochemical data are also useful in evaluating the source of minerals within a particular shale rock. Geochemical laboratory analysis and well logs are used in determining the critical shale reservoir properties stated above. Shale geochemical model, combined with geomechanical log and seismic data, is a very potent tool for reservoir evaluation and for identification and characterization of individual reservoir facies distribution, which is critical to understanding and predicting the potential for gas production from the reservoir and for putting in place optimal plans for economic recovery of gas from these unconventional resources.

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