# Sneha Rani. Ph.D.

Current Address: Dhanbad, Jharkhand, India

Phone: (+91) 8348521247 Email: snehatewary@gmail.com

https:www.linkedin.com/in/sneha-rani/

# **PROFESSIONAL SUMMARY**

- Resourceful scientist and innovative environmental engineer with 3 years of experience in chemical engineering, environmental management, climate change and sustainability that resulted in development of 2 new protocols
- Strong leadership skills and managing research professionals on collaborative projects leading to 9 publications and secured \$100,000 in lab grant funding, with 1 year of consulting experience
- Excellent communication skills as demonstrated by presenting research findings at various conferences/workshops and reviewed more than 10 manuscripts submitted in reputed journals

# **PROFESSIONAL EXPERIENCE**

## **Post-Doctoral Researcher**

Jun 2018 - Aug 2019

Universiti Teknologi PETRONAS, Malaysia

- Managed and executed high-throughput projects by presenting quarterly weekly project status to meet milestones and authored 3 peer-reviewed publications
- Characterized and investigated shale rock properties using advanced instrumental techniques with the purpose of identifying potential CO<sub>2</sub> sequestration sites; 1 manuscript in progress
- Accelerated innovation as demonstrated by the development of process for CO<sub>2</sub> separation using spent shale obtained from oil shale extraction, resulted in 1 patent application
- Experienced communicator, as demonstrated by presenting research data in 2 short-courses; Mentored and advised 3 undergraduate students to use high-pressure Adsorption Isotherm Setup
- Engaged in a collaboration with 4 international colleagues to deliver technology to a customer in Malaysia to increase yield of shale gas extraction by 50 60%

# **Sustainability Expert | Consultant**

Mar 2018 - Mar 2019

EPIC Sustainability Services Private Limited, Bengaluru

- Consultation for implementation of Carbon Capture Storage (CCS) projects under Clean Development Mechanism (CDM) project to 2 UNFCCC auditors
- Delivered expertise and knowledge in CCS and implementation of CO<sub>2</sub> storage in 3 different energy sectors in Indian context

Research Associate

Jul 2016 – Oct 2017

Dept. of Mining Engineering, Indian Institute of Technology Kharagpur

- Integrated techniques and executed experiments autonomously and in a team on gas adsorption and diffusion using shale samples; resulted in 3 reports and 1 publication
- Analyzed data statistically with 5 linear and 1 non-linear error analysis methods using Microsoft Excel and SPSS. Managed literature information and delivered 2 research proposals

- Confident public speaker, communicated research results at 1 national conference and 2 workshops
- Used business acumen to prepare and review 3 project proposals aligned with the budget requirement for different funding agencies with amount ranging upto \$150000

# **EDUCATION**

Ph.D. in Engineering. Indian Institute of Technology Kharagpur (Thesis: Sorption and Pore-Characterization of Indian Shale Samples) 2017

MTech in Environmental Science & Engineering. IIT (ISM) Dhanbad (Thesis: Inventorisation of Fugitive Methane Emissions from Oil & Natural gas activities in India) 2011

BE in Chemical Engineering. Visvesvaraya Technological University, Karnataka (Thesis: Life Cycle Assessment of Bio-Diesel using Jatropa Curcas in India)

2009

## **SCIENTIFIC EXPERIENCES**

- Reviewer for Fuel, Journal of Natural Gas Science and Engineering, AAPG Bulletin, Environmental Progress & Sustainable Energy and Environmental Technology and Innovation Journals, etc.
- Developed protocol for conducting volumetric adsorption experiments.

# **TECHNICAL EXPERTISE**

- Experience in CDM project for CCS, GHG inventory, LCA, sustainability reporting and EIA
- Expertise in energy sector and climate change
- Demonstrated Expertise in Adsorption Mechanism with use of artificial (such as zeolite) and natural materials
- R&D Experience in micrometer/nanometer structural surface characterization techniques
- Excellent knowledge of upstream sector for oil and gas reserve
- Managing Shale Gas PRF project funded by PETRONAS
- Shale gas reservoir, petrophysics, coalbed methane, rock characterization, H<sub>2</sub> storage & CO<sub>2</sub> storage in subsurface
- Familiarity with statistical analysis and numerical modeling
- Experience in micro/ macro-structural characterization techniques of porosity and transport properties (like: Electrokinetic Analyzer, SEM, GC, XRD, etc.)

# **SOFT SKILLS**

- Project management
- Quantitative and Statistical analysis
- Excellent business and technical sense
- Strategic planning and thinking
- Fundraising and Grant Writing
- Scientific writing
- Delivering high-level presentations
- Sound knowledge of using scientific software like Origin, SPSS, Xpert-High Score Plus, Matlab, HYSYS, MOD-FLOW

# **PUBLICATIONS**

- Rani, S., Padmanabhan, E., Bakshi, T., Prusty, B.K., Pal, S.K, CO<sub>2</sub> sorption and rate characteristics in micropores of shales. Journal of Natural Gas Science & Engineering 2019
- Rani, S., Prusty, B.K., Padmanabhan, E., Pal, S.K. Applicability of various adsorption isotherm models on adsorption of methane and CO<sub>2</sub> on Indian shales. Environmental Progress & Sustainable Energy 2019
- Rani, S., Padmanabhan, E., Prusty, B.K. Review of gas adsorption in shales for enhanced methane recovery and CO<sub>2</sub> storage. Journal of Petroleum Science and Engineering 2019
- Rani, S., Prusty, B.K., Pal, S.K. Adsorption kinetics and diffusion modeling of CH₄ and CO₂ in shales. Fuel 2018
- Rani, S., Prusty, B.K., Pal, S.K. Comparison of void volume for volumetric adsorption studies on shales from India. Journal of Natural Gas Science & Engineering 2015
- Rani, S., Prusty, B.K., Pal, S.K. Methane adsorption and pore characterization of Indian shale samples. The Journal of Unconventional Oil and Gas Resources 2015
- Basanta K. Prusty, Sneha Rani, Samir K. Pal, Aditya K. Patra. 2013. Gas Shale as a Source of Energy – An Overview. Indian Journal of Power and River Valley Development. II ISSN 0019-5537. Vol. 63, No. 11-12, Nov-Dec 2013

# **Book Chapter**

 Rani, S. (2019). Clay Mineralogy: Carbon Stabilization as a result of Interaction between Soil and Organic Matter Clay Mineral. Invited Book Chapter Submitted. Springer Published Book 'Titled "Soil Carbon Stabilization to Mitigate the Climate Change"

## CONFERENCES

- Basanta K. Prusty, Tuli Bakshi, Sneha Rani, Samir K. Pal. 2017. Characterisation of Damodar valley shales for exploration and exploitation of shale gas. International Conference on NexGen Technologies for Mining and Fuel Industries (NxGnMiFu). 15-17<sup>th</sup> February 2017, New Delhi, India
- Basanta K. Prusty, Sneha Rani, Samir K. Pal. 2013. Adsorption Behavior of Coal and Shale from Jharia Coalfields- A comparison. International Conference on Coal & Energy-Technological Advances & Future Challenges (CETAFC). 15-17<sup>th</sup> December 2013. Kolkata, India

# **INVITED PRESENTATIONS**

- S. Rani. Short Course on "High Pressure Gas Sorption in Shale for Unconventional Gas Recovery", IAS, Universiti Teknologi PETRONAS, 22<sup>nd</sup> April, 2019
- S. Rani. Short Course on "Shale Gas Reservoirs Potential for Hydrocarbon Recovery & CO<sub>2</sub> Storage", Universiti Teknologi PETRONAS, 17<sup>th</sup> April, 2019
- S. Rani and B.K. Prusty. CO<sub>2</sub> Sequestration in Coal seams and Shale gas resource systems.
   Short Term Course on "Coal Mine Methane & Shale Gas Technology", Indian Institute of Technology Kharagpur, 25-27<sup>th</sup> April, 2017
- Sneha Rani. Sorption and Pore-Characterization of some Indian Shales. Great Step 2016, organized by Society of Mining Engineers, Indian Institute of Technology Kharagpur, 1<sup>st</sup> October, 2016
- S. Rani, Basanta K. Prusty, Samir K. Pal. Comparing the applicability of Langmuir isotherm model for Coal and Shale from Jharia Coalfields. National Hindi Seminar on Coal-based Gas Industry-Its problems and prospects, organized by CSIR-Central Institute of Mining and Fuel Research, Dhanbad, 11<sup>th</sup> May, 2015
- S. Rani. Coalbed Methane Extraction-An Environmental Friendly Technology. Seminar, organized on World Environment Day by EMG Central Institute of Mining and Fuel Research, Dhanbad, 5<sup>th</sup> June, 2011

# **INDUSTRIAL TRAINING**

- Successful completion of Core Lab Instruments Model: SMP 200 Shale Matrix Permeameter Hands on Operation Training by Hisco (Malaysia) Sd. Bhd. (Dec, 2018)
- Successfully completed the Swagelok Tube Fittings Installation Course (Certificate Number and Date: BOMBA-2012-K201, April 30, 2012)
- Attended summer school on 'Coalbed Methane Extraction and its Environmental Issues' at Molopo Energy India Private Ltd, Kolkata, India (from May – June, 2010)

# **FIELD EXPERIENCES**

- Worked as scientific investigator with Jharia Rehabilitation and Development Authority (JRDA) for Socio- Economic Survey of Jharia, Dhanbad, Jharkhand for Rehabilitation (from July 2010 December 2011)
- EIA of Open-cast Coal Mining Projects of Jharia Coalfied in Jharkhand (April 2010)
- Hazard Identification & risk Assessment (HIRA) of Lodna underground and Ena fire mine, Jharia and Chandrapura Thermal Power Station, Jharkhand

# POSITIONS OF RESPONSIBILITY

- Organizing committee member for International Conference of 'Safety in Mines Research Institutes & Mine Safety Exhibition' (ICSMRI, 2011), New Delhi, India
- Active member of Breakthrough Science Society, IIT Kharagpur Chapter
- Raised funds for West Bengal (2015) and Uttarakhand (2013) flood affected victims
- Worked in audience and participant management team for 60<sup>th</sup> Annual Convocation held on 26<sup>th</sup>
   July, 2014 at IIT Kharagpur. Event involved dealing with 5000 guests from around country
- Organized Research Scholar's Day, 2013, Department of Mining Engineering at IIT Kharagpur

## **AFFILIATIONS & HOBBIES**

- Awarded First prize for poster presentation by the Minister of Petroleum and Natural Gas, India during International Shale Gas and Oil Workshop, 2016, New Delhi
- Attended IEAGHG International Interdisciplinary Carbon Capture Storage (CCS) Summer School held at The University of Texas, Austin, USA (2014)
- Attained Best Performer for Poster presentation, Research Scholar's Day 2015, IIT Kharagpur 2015
- Mentored eight undergraduate students and two postgraduate researchers
- Participated in inter-hall choreography competition, IIT Kharagpur (2012 2013)
- · Hiking, badminton and cycling

# **REFEREESS**

Prof. BK Prusty

Associate Professor

Department of Mining Engineering, IIT Kharagpur, Kharagpur: 721302, West Bengal Email: bkprusty@gmail.com, Phone: +91-9474065042

Prof. SK Pal

Professor

Department of Mining Engineering, IIT Kharagpur, Kharagpur: 721302, West Bengal Email: pal.samir09@gmail.com, Phone: +91-9609166184

Dr. Eswaran Padmanabhan

Associate Professor

Universiti Teknologi PETRONAS

Bandar Seri Iskandar, Perak, Malaysia

Email: eswaran\_padmanabhan@utp.edu.my, Phone: +60-123756955



# **Applicability of Various Adsorption Isotherm** Models on Adsorption of Methane and CO<sub>2</sub> on **Indian Shales**

Sneha Rani , a Basanta K. Prusty, Eswaran Padmanabhan, a and Samir K. Palb

<sup>a</sup>Institute of Hydrocarbon Recovery, Universiti Teknologi Petronas, Seri Iskandar Perak 32610, Malaysia; snehatewary@gmail.com (for correspondence)

<sup>b</sup>Department of Mining Engineering, Indian Institute of Technology, Kharagpur 721302, India

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To produce natural gas (methane) and simultaneously sequester CO<sub>2</sub> in unconventional geologic reservoirs such as gas shale, coalbeds and so on, it is necessary to understand the adsorption behavior of methane and CO<sub>2</sub> in these reservoir formations. In this article, adsorption behavior of methane and  $CO_2$  on shale samples from Gondwana Basin and KG Basin of India are studied. Adsorption experiments are conducted on as-received shale samples from these basins at a temperature of 313 K to a maximum equilibrium pressure of approximately 9 MPa for methane and 6 MPa for CO<sub>2</sub>. The methane and CO<sub>2</sub> adsorption data are applied to test the applicability of Langmuir, Dubinin-Polanyi, BET, and Ono-Kondo models. A comparison of these models is performed using linear and nonlinear Chi-squared methods. It was observed that Dubinin-Astakhov equation was the most accurate adsorption isotherm model for adsorption of methane and CO2 on tested shales. Further, the better fitting by Dubinin-Polanyi equation over BET, Langmuir, and Ono-Kondo models suggest that the mechanism of volume filling may be applicable during the adsorption of methane and CO2 on shales. The preferential adsorption of methane and carbon dioxide on Pakur, KG, and Salanpur shales were investigated. The Pakur shale had CO<sub>2</sub>:CH<sub>4</sub> adsorption ratio ~1. © 2019 American Institute of Chemical Engineers Environ Prog, 2019

Keywords: modeling, adsorption isotherm models, adsorption capacity

#### INTRODUCTION

Unconventional resources like coalbeds, gas shales, tight gas sands, and so on have become important energy source due to the depletion of conventional energy resources. Natural gas production from coalbeds has increased significantly over the decade in USA, China, Australia, and Canada. Advances in drilling technology and recovery techniques have boosted natural gas production from gas shales in USA over the last decade [1,2]. With the success of shale gas development in USA, interest on gas shale as a reservoir has increased greatly throughout the world. Countries like China, Australia, Canada, Brazil, Argentina, and many Eastern European countries such as Poland, are also exploring shale gas resource to boost their domestic gas production [3].

Unconventional reservoirs such as gas shales also provide a huge sink to sequester CO2 which is the most abundant

greenhouse gas. Disposal of CO<sub>2</sub> in gas shale formations may help achieve the twin objectives of sequestration of greenhouse gas and enhanced recovery of methane from gas shale formations. Sequestration in gas shale is promising because of the economic benefits due to the associated methane production [4,5]. Gas storage mechanism in the shale formations is different from that of conventional reservoirs. The adsorbed gas accounts for 40-50% and free gas may account up to 60% of the total gas content of shale [6]. Since adsorption plays a significant role in storage of gas in gas shale reservoirs, it is important to understand the adsorption behavior of shales. Usually, adsorption of gas on microporous solids (coals or shales) follows Type I curve [7,8]. Previous literature has reported that for many shales, methane adsorption exhibit monolayer adsorption represented by a Type I isotherm [9-13]. However, deviations from Type I isotherm have also been reported for some Jurassic and Devonian shale samples from Canada [8]. Various adsorption isotherm (AI) models have been used to mathematically represent methane and CO2 adsorption data on shales. The best AI models giving good fit to adsorption data of shales can be used by industry for developing a shale gas reservoir simulator. Adsorption modeling may also provide information on possible adsorption mechanism on shales like: monolayer/multilayer adsorption or pore volume filling.

Adsorption modeling is an important part of adsorption studies. Adsorption models are used in shale gas reservoir simulators for forecasting reservoir production potential. Accurate adsorption modeling will lead to more precise forecasting by reservoir simulator. Various AI models such as: Langmuir, Dubinin-Polanyi (D-P), and Brunauer, Emmett and Teller (BET) have been used for modeling adsorption on sedimentary rocks. Extensive literature is available on applicability of these AI models on coal [2,4,14–17]. In case of shales, previous studies mostly focused on application of Langmuir model to the experimental methane and CO2 adsorption data [9-13,18-23]. Some researchers have also reported the applicability of BET and D-P models that are based on the mechanism of multilayer adsorption or pore-volume filling, respectively [24–27]. Recently few authors have applied the Ono-Kondo model to describe methane adsorption data on shales [27,28]. The Ono-Kondo model was initially developed to explain density differences in a gas-liquid interface [29]. Later Ono-Kondo model was applied on studies related to gas adsorption on microporous solids [30-34]. Among all the AI models, Ono-Kondo model has advantages which include its ability to describe adsorption data for

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## Full Length Article

# Adsorption kinetics and diffusion modeling of CH<sub>4</sub> and CO<sub>2</sub> in Indian shales

Sneha Rani, Basanta K. Prusty\*, Samir K. Pal

Department of Mining Engineering, Indian Institute of Technology, Kharagpur 721302, India



## ARTICLE INFO

Keywords:
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Methane
CO<sub>2</sub>
India
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Modeling
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## ABSTRACT

The concept of increased gas (methane) recovery with simultaneous  $CO_2$  sequestration in unconventional reservoirs like gas shales has been studied in the past few years. Diffusion is the main transport mechanism in shale gas reservoir. Understanding the methane and  $CO_2$  diffusion properties of shales and its modeling is important for planning successful methane recovery and  $CO_2$  sequestration in these reservoirs. Methane and  $CO_2$  adsorption kinetic studies were carried out at four different pressure steps (in the range of 3.5–8.9 MPa for  $CH_4$  and 2–6 MPa for  $CO_2$ ) to investigate their diffusion behavior on two shale samples (Pakur and Salanpur) from Damodar Valley Basin, India. The sorption kinetic data was modeled using unipore model and modified unipore model (MM). The unipore model is giving good match with experimental sorption kinetics data up to a fractional uptake of 62–92% for methane and 62–88% for  $CO_2$ . The MM model is giving very good match up to the fractional uptake of 78–99% for methane and 77–98% for  $CO_2$ . It was observed that the MM model is giving better fit than that of unipore model for both gases for the entire pressure range. Thus it can be suggested that MM model is a better model to represent the diffusion of methane and  $CO_2$  in shales.

## 1. Introduction

Anthropogenic emission of greenhouse gases particularly,  $CO_2$  is believed to be responsible for the global climate change. Carbon sequestration has been identified as one of the technological alternatives for reducing  $CO_2$  emission from the atmosphere. Depleted oil reservoirs, saline aquifers and gas-hydrate reservoirs are some of the potential sites for carbon sequestration. The unconventional reserves such as depleted gas shales can also provide a huge sink to sequester  $CO_2$  [1]. Disposal of  $CO_2$  in coal/shale formations may help in achieving the twin objectives of sequestration of the greenhouse gas and enhanced gas recovery (EGR) specifically methane from the gas shale formations. Flow and storage of  $CO_2$  in gas shale seems to be very promising because of the expected economic benefits due to the associated methane production [2]. To optimize this process it is necessary to understand in detail the storage mechanism and flow properties of the shale rock formation.

Gas transport in shales can be explained by dual- or triple-porosity models [3,4]. King et al. [5] states that shale reservoir has a dual-porosity behavior, and is composed of primary porosity and secondary porosity system. The micropores in the matrix of shales constitute the primary-porosity system. The secondary-porosity system consists of cleats and other natural fractures (macropores). The flow of gas in shale reservoirs takes place mainly due to three mechanisms, i.e. desorption, diffusion and viscous flow [6,7]. Depending on the characteristics of the reservoir and gas type, these three mechanisms control the flow. The

gas flow in primary- and secondary-porosity system is usually controlled by Fick's law of diffusion and Darcy's law respectively.

The knowledge of gas transport properties of shales is important for successful methane recovery and CO2 sequestration in shale gas reservoirs. Transport of gas in shale occurs in two stages. In the first phase, diffusion is faster within macropores where molecular diffusion occurs which is controlled by Fickian diffusion. In the second phase, slower diffusion occurs in micropores, i.e. dominated by Knudsen diffusion, where molecular and pore wall collision dominates [8]. The internal surface area of micropores holds a significant part in shale matrix. Although micropore diffusion is considered a single process, it is usually a combination of three types of diffusion. These are namely Knudsen diffusion (where molecule-wall collisions dominate), surface diffusion (transport through physically adsorbed layer) and bulk diffusion (molecule-molecule collisions dominate) [9]. Diffusion is one of the main mechanisms of transport of gas in a shale gas formation that controls the rate of recovery of gas from the gas shale reservoir [10]. The rate of flow of gas from the matrix (micro- and meso-pores) to the fractures (macropores) in shale gas reservoirs is controlled by diffusion. Some of the previous studies, suggest that pore structure has important role in storage and transport of gas in the shale matrix [11,12]. Hence the study of gas transport in shale is important for understanding the gas flow in a shale-gas system.

E-mail address: bkprusty@mining.iitkgp.ernet.in (B.K. Prusty).

<sup>\*</sup> Corresponding author.

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# CO<sub>2</sub> sorption and rate characteristics in micropores of shales

Sneha Rani<sup>a,\*</sup>, Eswaran Padmanabhan<sup>a</sup>, Tuli Bakshi<sup>b</sup>, Basanta K. Prusty<sup>b</sup>, Samir K. Pal<sup>b</sup>



#### ARTICLE INFO

Keywords:
Shale
Adsorption behavior
Sorption kinetics
Pore characteristics
CO<sub>2</sub>
Micropores.

Abstract: Carbon dioxide adsorption behavior and sorption kinetics of two shales from Damodar valley basin, India were experimentally investigated by volumetric method at 313 K and up to 6 MPa. Langmuir, Dubinin-Astakhov, Dubinin-Radushkevich and Brunauer-Emmett-Teller equations were used to model experimental adsorption data. The present study was also aimed at characterizing pore-structure and composition of shale samples. The two shales were found to be rich in organic matter with total organic carbon content to be more than 5% indicating fair to good source rocks. Modeling of  $CO_2$  adsorption data showed that BET and D-A models gave better fit compared to Langmuir model. Pore volume data obtained from mercury intrusion capillary porosimetry is consistent with that of low pressure  $(N_2$  and  $CO_2)$  adsorption for pore sizes > 10 nm for SLP sample. In case of PAK sample, pore size data obtained from mercury intrusion and low pressure adsorption drifted apart for pore sizes > 10 nm. PAK shale displays pore structure in mesopore range with modes approximately at 3 nm and 4 nm. The SLP sample has bimodal pore structure with one peak in micropore range (SLP - 1.17 nm) and other peak at  $\sim 4$  nm (mesopore range). The  $CO_2$  diffusivity determined from adsorption rate data measured at subcritical pressures was in the range of  $1.0364 \times 10^{-8}$  to  $2.6588 \times 10^{-8}$  for PAK shale and  $1.0624 \times 10^{-8}$  to  $1.6343 \times 10^{-8}$  for SLP shale. Further, it can be suggested that during initial time,  $CO_2$  diffusion in shale is a non-steady process and later transforms to steady-state mechanism.

## 1. Introduction

Greenhouse gases principally, carbon dioxide, released from anthropogenic emissions is considered to be accountable for global climate change. CO2 concentrations have increased by three fold from 280 ppm - 385 ppm to 404 ppm in the year 2016 and methane concentration has doubled since preindustrial era (IPCC Climate Change, 2007; IEA, 2016). Intergovernmental Panel on Climate Change (IPCC) suggests importance for an instant reduction in CO2 emissions (50-70%) to stabilize global CO2 concentrations of 1990 levels by 2100 (IPCC Report, 1995). IPCC predicts rise in global temperatures by 1.1-6.4 °C by 2100, if proper mitigation measures are not undertaken (Metz et al., 2005; Park, 2007). Carbon sequestration in geological media can be recognized as an option of minimizing CO2 emission from the atmosphere. Depleted oil reservoirs, saline aquifers and gas-hydrate reservoirs have been identified as some of the potential sites for carbon sequestration (Aminu et al., 2017). The unconventional reserves such as depleted gas shales can also provide a huge sink to sequester CO<sub>2</sub> (Kang et al., 2011). Disposal and storage of CO2 in coalbed and gas shale seems to be a promising alternative as a result of expected economic benefits due to the associated methane production (Harpalani et al.,

### 2006).

Recently, different countries have adopted simultaneous injection of CO2 in shale gas reservoir to achieve increased methane recovery. Kentucky Geological Survey conducted a pilot-scale study for CO2 injection in Devonian Ohio black shales in Eastern Kentucky. An estimate of 87 tons of CO<sub>2</sub> was injected during this injection program which was later terminated due to a packer failure (Nuttall et al., 2005). A pilotscale 'huff-and-puff' method of CO2 injection was conducted on Chattanooga Shale formation in Morgan County, Tennessee to investigate enhanced methane recovery. An estimate of 510 tons of CO2 was successfully injected into the shale formations. On completion of injection stage, well was closed such that injected CO2 attains equilibrium. After injection stage, well was resumed for normal production. The monitoring results revealed considerable increase in gas flow rate in the initial few months of flowback stage. This program was successful in increasing methane recovery by storing CO2 in targeted shale formations (Louk et al., 2017). In order to optimize the process of simultaneous CO2 injection and enhanced methane recovery in shale gas reservoirs, it is necessary to understand in detail the gas storage parameters and flow properties in these shale rock formations.

CO2 sequestration potential and enhanced methane recovery of

E-mail address: snehatewary@gmail.com (S. Rani).

<sup>&</sup>lt;sup>a</sup> Institute of Hydrocarbon Recovery, Universiti Teknologi PETRONAS, Perak 32610, Malaysia

<sup>&</sup>lt;sup>b</sup> Department of Mining Engineering, Indian Institute of Technology Kharagpur, Kharagpur 721302, India

<sup>\*</sup> Corresponding author.

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# Methane adsorption and pore characterization of Indian shale samples



Sneha Rani, Basanta K. Prusty\*, Samir K. Pal

Department of Mining Engineering, Indian Institute of Technology, Kharagpur 721302, India

#### ARTICLE INFO

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Keywords: Adsorption Methane India Pressure Shale

#### ABSTRACT

Understanding adsorption behavior of methane in shale is important for predicting the gas reserve and evaluating reservoir potential. This paper presents the methane adsorption behavior of three gas shale samples of Gondwana and KG basin of India. Adsorption experiments are conducted on as-received samples at a temperature of 40 °C to a maximum equilibrium pressure of approximately 9.5 MPa. The methane adsorption data are applied to test the applicability of Langmuir isotherm model. It was observed that the experimental adsorption data for Parbatpur and KG shale samples did not follow the Langmuir isotherm model, with deviation from the model value more than 10%. Although the experimental adsorption data of Salanpur sample broadly followed the Langmuir model, the deviation from the model value was more than 5%, implying the Langmuir model is not very accurate. Pore characterization study was also carried out to understand the pore structure of the shale samples. The pore characterization suggested that porosity of Indian gas shales are dominated by meso- and macro-pores.

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#### Introduction

With rise in energy demand, conventional natural gas resources are getting depleted. In order to meet the increased energy demand, unconventional resources like gas shale are being explored. Commercial production of gas shale has been successful in the USA. Shale gas currently contributes to approximately 17% of the total domestic gas production in the USA (Bai et al., 2013). The shale gas success story in the USA has encouraged other countries like Canada, Poland, Australia, China, Argentina, and India to explore the potential of shale gas. In the present study an attempt has been made to understand the adsorption behavior of methane on Indian shales.

Shales are fine-grained sedimentary deposits. The shale consists of both organic carbon and inorganic minerals. Natural gas found in shale is referred to as shale gas. The shale gas typically consists mostly of methane (>94%), lesser amounts of higher hydrocarbons (ethane, propane and butane) and traces of CO<sub>2</sub> and N<sub>2</sub> (Kalkreuth et al., 2008). Storage mechanism of gas in shale is different from that of conventional reservoirs. The gas in shale is mainly available in two forms: adsorbed state on the surface area of pores in the organic matrix, and in free state in the pores of the clay minerals (Kuila and Prasad, 2011). Adsorbed gas accounts for 40–60% of the total gas content in shale. The free gas may account up to 60% of the total gas content of shale (Lewis and Hughes, 2008). Unlike

Since a significant fraction of the gas in shale is stored by adsorption mechanism, understanding adsorption behavior of gas shale is important in developing gas-in-place estimates as well as predicting the production rate from a shale reservoir (Chareonsuppanimit et al., 2012). Establishing adsorption isotherm for methane on shale is one of the critical steps in estimating economic potential of gas shale reservoir. Various adsorption isotherm models such as Langmuir, BET, Dubinin-Polanyi, Freundlich model etc. are used to model the adsorption of gas in different solid adsorbents. Among these, the Langmuir isotherm model is the most commonly used for sedimentary formations like coal and shale. Since the Langmuir isotherm model has been used extensively for coal, it is of interest to see whether this model is also applicable in case of shale. The main objective of this paper is to study the adsorption behavior of gas shale samples from India and to investigate the applicability of Langmuir isotherm model on methane adsorption data on Indian shale samples.

Literature review

Langmuir isotherm model has been used to describe methane adsorption data on coals and some gas shales. Although

coal, where adsorption of gas takes place only on the organic portion, adsorption of methane in shale takes place both on the organic as well as the mineral matter (mostly on the clay minerals). The organic matter contributes to approximately 90% of the methane adsorption and rest (approximately 10%) of the adsorption takes place over the mineral matter (Ross and Bustin, 2007).

<sup>\*</sup> Corresponding author. Tel.: +91 3222 283700. E-mail address: bkprusty@mining.iitkgp.ernet.in (B.K. Prusty).

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# Review of gas adsorption in shales for enhanced methane recovery and CO<sub>2</sub> storage



Sneha Rani<sup>a,\*</sup>, Eswaran Padmanabhan<sup>a</sup>, Basanta K. Prusty<sup>b</sup>

- <sup>a</sup> Institute of Hydrocarbon Recovery, Universiti Teknologi Petronas, Perak 32610, Malaysia
- <sup>b</sup> Department of Mining Engineering, Indian Institute of Technology, Kharagpur 721302, India

#### ARTICLE INFO

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#### ABSTRACT

The concept of increased methane recovery with simultaneous  $CO_2$  sequestration in unconventional reservoirs like gas shales has been studied extensively. A clear understanding of storage mechanism and geo-chemical characteristics of shale gas reservoirs is necessary for predicting the gas reserve and evaluating reservoir potential. The present article reviews literature on adsorption of methane and carbon dioxide on shale for the purpose of methane recovery with simultaneous  $CO_2$  sequestration in shale gas reservoirs. The objective of this article is to discuss the technical aspects related to gas adsorption and characterization (both composition and pore) concerning shale gas reservoirs. The various adsorption mechanisms, different adsorption isotherm types and shales as a microporous adsorbent are discussed. Using the published information in literature, methane and carbon dioxide adsorption in shales and its relationship with different geochemical parameters like organic matter content, mineralogy, pore-structure and moisture as essential controls for gas adsorption in shale are discussed. Studies that answer the concerns on effect of shale composition and pore characteristics on adsorption capacity of heterogeneous shale are also summarised.

#### 1. Introduction

Currently, global warming is a major challenge/concern faced by the scientific community across the globe. Geologic storage of  $\mathrm{CO}_2$  is being regarded as a promising technique of mitigating global warming (Pachauri and Reisinger, 2007). Shale formations can be probable option of storing  $\mathrm{CO}_2$  in productive shale gas reservoirs (NETL, 2012). Sequestration of  $\mathrm{CO}_2$  in gas shale formations holds an additional advantage of enhanced methane recovery/production which can help offset the cost of storage making it an economically viable alternative. Godec et al. (2014) suggested the potential of enhanced gas recovery (EGR) and storage of  $\mathrm{CO}_2$  in gas shales globally. The economic estimate is predicted to be 71 Tcm of enhanced methane recovery which could facilitate 280 Gt of  $\mathrm{CO}_2$  storage.

Gas shales are identified as unconventional reservoirs containing natural gas with large amounts reported in US and Canada (Montgomery et al., 2005; Jarvie et al., 2007; Chalmers and Bustin, 2008; Ross and Bustin, 2008). Barnett, Caney, Woodford, Fayetteville, Antrim, Ohio, New Albany and Lewis are some of the potential shale gas reservoirs in the US where natural gas has been exploited. These fine grained shales that produces hydrocarbon varies in wider range from mudstone, siliceous or carbonate to sandstone (Jarvie et al., 2007;

Montgomery et al., 2005; Curtis, 2002; Martini et al., 1996). Tight gas sands, coal and shale are some of the low permeability formations which are termed as unconventional gas reservoirs. Shale gas reservoirs are called unconventional systems as a result of smaller grain size, hydrocarbon being stored in adsorbed state and acting as source which results in formation of pore structure different from conventional systems (Wang and Reed, 2009; Ambrose et al., 2010; Sondergeld et al., 2010). The difference in geological framework separates unconventional hydrocarbon systems (such as shale gas) from the conventional hydrocarbon systems (Hill et al., 2007). A conventional hydrocarbon reservoir comprises of source rock, reservoir rock, seal, overburden, thermal maturity, migration, and formation of trap (Magoon and Dow, 1994). On the other hand, shale gas reservoir systems consist of source rock, trap and reservoir, in which shale acts as all three (Martini et al., 1998; Hill et al., 2007; Bernard et al., 2010; Glorioso and Rattia, 2012).

Shale gas is mainly a combination of majority of methane (> 94%), lesser amounts of higher hydrocarbons (ethane, propane and butane), traces of  $CO_2$  and  $N_2$  found in shale rock (Kalkreuth et al., 2008). The term "gas shale" is known as a fine-grained sedimentary rock which can store natural gas in the porosity system by adsorption (Law and Curtis, 2002; Bustin, 2005; Bustin et al., 2008). The origin (thermogenic/biogenic) and geochemical type (wet gas/dry gas) control the chemical

E-mail address: snehatewary@gmail.com (S. Rani).

<sup>\*</sup> Corresponding author.