1. **Project Title:** "Effect of pore structure of Indian gas shales on its methane and CO2 adsorption behavior"
2. **Duration in months: 36** Months

3. **Total Estimated Budget:** Rs. 1,08,56,000

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4.

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SECTION – B

1.0. Project Title: Effect of pore structure of Indian gas shales on its methane and CO_2 adsorption behavior.

2.0 Project Type:

- Basic research

3.0 Introduction and Review of Literature:

Natural gas consisting mostly of methane (and traces of higher hydrocarbons like ethane, propane, butane etc.) is stored in shale (gas shales) that is now considered as important unconventional reservoir. On the other hand, gas shale deposits can also be used as potential sinks for sequestration of CO_2 thus helping in managing the climate change. India has identified shale gas reservoirs for exploration and potential recovery operations. However, detailed exploration and geo-chemical characterization of our shale deposits are required in order to delineate the deposits for commercial recovery and CO_2 sequestration.

Shales are fine-grained sedimentary rocks which have been formed from the consolidation of beds of mud, clay or silt. The shales contain organic carbon that is known as kerogen and clay minerals such as: kaolinite, montmorillinite, illite, mica, etc. Gas storage mechanisms in shale are of two types:

1. Adsorbed gas on both organic matter and clays; and
2. Free gas stored in the pore volume (accounts for up to 60% of the total gas content)

Adsorption has important control on the recoverability and storage of gas in shales. Adsorption contributes to ~ 40-50% of the gas storage capacity of shales and is an important mechanism of storage. Adsorption is the dominant storage mechanism for unconventional reservoirs like coalbed also. However, the difference between coal and gas shale is that shale is a low organic matter rock, thus, the amount of adsorption may be less in case of shale. Moreover, shale occurs at greater depth (up to 4000 m). At such depth, the reservoir temperature is very high (up to 140 ^{0}C) and the reservoir pressure is also very high (up to 400 bar). Adsorption behavior on low organic rock at high temperature and high pressure condition may be different compared to adsorption on coal at moderate temperature (up to 50^{0}C) and moderate to high pressure (100-200 bar). Understanding of adsorption behavior of shale is thus very important for calculating shale gas potential and recovery. The adsorption property is usually studied by conducting adsorption isotherm experiment.

The gas shale consists of two main parts: the organic part, and the clay minerals. The organic matter of the shale contains a lot of pores mostly micro- and nano-pores. These pores provide sites for adsorption of gas. Adsorption of methane occurs mostly on the micropores/ nanopores of organic matter. The inorganic portion consisting of clay minerals also contain lot of pores which stores gas in compressed and free state. A small fraction (< 10%) of the adsorbed gas also resides on the clay mineral surfaces. The clay minerals also play a significant role in imparting micro-porosity and ability to hold adsorbed gas on their grain surfaces. The pores and the pore characteristics of shales have critical effects on the adsorption capacity, gas storage and also on the flow of gas in shales. Pore characterization studies of some gas shale rocks are available for some of the American shale plays. However, such studies are not available in the public literature for Indian gas shales. It is therefore important to study the pore characteristics of some of the Indian gas shale formations and investigate the correlation between the adsorbed capacities with pore characteristics for Indian gas shales.

Definition of the problem

Adsorption studies are important for gas shales not only from the gas storage but also for the recoverability point of view. Limited literatures about adsorption property of shales from the USA are available in the public domain. However, adsorption studies on Indian gas shales are very rare. Moreover, Indian gas shales are different compared to shales from other countries. Therefore, it is important to characterize the adsorption behavior of Indian gas shales by carrying out adsorption studies. Further, shale gas is composed of methane and other heavier hydrocarbons. The shale will have different sorption affinity for different gases. It is important to study the preferential affinity of shale towards different gases such as methane, CO_2. Moreover, the adsorption property of shale for more than one gas i.e. a gas mixture should be studied by conducting multi-component gas mixture.

Adsorption modeling is important to determine parameters that can be used in the production simulation software. In case of coalbed methane, where Langmuir adsorption isotherm is mostly used, the Langmuir volume and Langmuir pressure are used in the CBM production simulators. However, for shale gas, the adsorption literature is limited, and the appropriate adsorption model has not been agreed upon by researchers. Therefore, it is important to identify or develop the most appropriate adsorption isotherm model for Indian gas shales so that the adsorption parameters can be suitably incorporated in the shale gas production simulator.

Pore characteristics of the gas shales control the storage as well as the transport property of the shale rock. American shales usually contain micro and nano-pores. The pore size with a critical effect on permeability and diffusion (of methane), sometimes becomes the limiting factor for the gas production. The transport of the gas cannot be modeled without characterizing the pore structure and without understanding the flow phenomenon in the micro-pores of the shales. Therefore it is very much important to characterize the pore structure of the Indian gas shales in order to ascertain the potential/deliverability of shale gas from the Indian shale reservoirs.

Literature review

Adsorption of gas on shale takes place by the mechanism of physical adsorption (Kang et al., 2011). The adsorbed gas is mostly present in the micropores of the organic matter and a small amount is also present within the clay minerals. The adsorbed gas ranges from 40% - 50% of the total gas content of the shale. Free gas may account up to 60% of the total gas content of shale (Lewis and Hughes, 2008). Since adsorption plays a significant role in the storage of gas in shale reservoirs, it is important to understand the adsorption behavior of shales. Unlike 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).

The storage and flow properties of gas shale formation are mainly controlled by the geo-chemical characteristics of the formation. Apparently total organic carbon content (TOC), maturity, mineral matter, and porosity are some of the important controlling parameters that play a crucial role in adsorption of gas on shales. The adsorptive capacity of shale is linked to the composition and pore structure (Ross and Bustin, 2009). Most of the adsorption of methane occurs on the micropores/nanopores of organic matter. The clay minerals also hold small amount (10%) of the total adsorbed gas and thus contribute to the gas content of shale (Ross and Bustin, 2007). Ross and Bustin (2009) have referred to the dependence of adsorbed capacity with the organic and inorganic composition of American shales. It may be of interest to explore whether such dependence exists for the Indian shale formations. Therefore, studying the organic matter and mineral composition of the shale is very important for characterization of the shale rock.

The heterogeneous nature of shales containing wide variety of pore sizes ranging from micro-, meso-, and macro-pores makes the pore-structure complex. Understanding the pore-structure of shales is essential because the adsorbed gas found in shale is mostly present in the micropores. Ross and Bustin (2009) reported positive relationship between adsorption capacity and porosity. They also observed that shales with large micropore volumes had higher adsorption capacity. Kuila and Prasad (2011), reported dominance of mesopores in some of the American shales. The flow behavior of gas in shales is also dependent on the pore characteristics such as: pore size, pore size distribution and their interconnectivity. Therefore, understanding the porosity and pore-structure of shale is extremely important for the pore-characterization of shales.

The potential of CO_2 sequestration and enhanced recovery of methane from the gas shale formations will depend on the preferential sorption behavior of shale for CO_2 over methane (Vermylen, 2011). Studies suggest gas shale has the ability to adsorb more CO_2 compared to methane due to its preferential sorption behavior. Nuttall et al. (2005) observed that CO_2 is adsorbed approximately 5 times more than that of CH_4 for Devonian black shales. Further, the CO_2 sequestration potential of a gas shale formation may be controlled by some of the geo-chemical characters of the shale formation. Total organic carbon (TOC) may be a major controlling parameter in CO_2 sequestration (Kang et al. 2010). As discussed earlier, that 90% of the adsorbed gas is present in the organic matter. Hence, the shale formations with higher total organic carbon (TOC) may act as a suitable site for CO_2 sequestration.

3.1 Current status of work being done in other Institutions and Industries in the country:

NIL

3.2 Current status of work being done on International scale:

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7. Nuttall, B.C., Eble, C.F., Drahovzal, J.A., Bustin, R.M., 2005, Analysis of Devonian Black Shales in Kentucky for Potential Carbon Dioxide Sequestration and Enhanced Natural Gas Production. Kentucky Geological Survey, University of Kentucky, Lexington, Kentucky.

3.3 Details of previous work and ongoing work of PI and Indian Institute of Technology Kharagpur in this field and expertise available with PI/Group/Institution/Organization:

1. Assessment of sealed off areas at Moonidih mine, India. *Funded by SIUC and USEPA.*
2. An investigation on adsorption characteristics of Indian coals and to ascertain recoverability of CBM from deep seated coal and lignite resources. *Funded by Coal India Limited.*
3. Greenhouse Gas Recovery from coal mines and unmineable coal beds and conservation to energy. Funded by European Union.
4. CO_2 Sequestration in Abandoned Coal Mines - A Feasibility Study. Funded by DST, Government of India.
5. Study of Enhanced Methane Recovery and Carbon Sequestration by Carbon Dioxide Injection to Coalbed Methane Reservoir: Sponsored by DOE, USA.
6. Viability of CO_2 Sequestration and Methane Production in Illinois Coal; sponsored by Illinois Clean Coal Institute.
7. Gas Flow Characterization of Illinois Coals; sponsored by Illinois Clean Coal Institute.