SHALE CHARACTERIZATION USING X-RAY DIFFRACTION

By

ALI SHEHZAD BUTT

Submitted in partial fulfillment of the requirements
for the degree of Master of Engineering

Major Subject: Petroleum Engineering

at

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DEDICATION

I dedicate this project wholeheartedly to the Almighty God for giving me life, strength and the
courage to pursue this program. Furthermore, I dedicate it to my dear parents, brothers and my
entire family for their unconditional support. Thank you.
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Shale gas has abnormal reservoir characteristics and it has very low permeability like in nano-darcy ($k < 0.1 \text{ md}$). Shale gas formation also shows the unique behavior because it store gas on the matrix surface. World’s conventional reservoirs are depleting at an alarming rate and we must find alternate sources to keep the supply undisturbed. The large volume and attractive gas prices brings unconventional resources into the forefront of our energy future. Tight gases exist in the underground reservoirs and have huge potential for production. We use hydraulic fracturing and directional drilling to take production from these low permeability reservoirs. By using these technologies, unconventional resources are moving to economically viable sources of natural gas.

This study shows how we can characterize different minerals in shale with the help of X-ray diffraction. X-ray diffraction is widely used for the phase identification of a crystalline material and can provide valuable information. Modern instrumentation and automation gives fast results. Results are sensitive to variations in sample preparation as well as to irregularities in the sample. Knowing the clay mineral composition of the shale can be useful in drilling. It can tell us whether swelling clays (smectite, bentonite) are present or not. Swelling clays can get sticky, ball up around drill bits, cause headaches for drilling contractors and increase capital cost.

A sample of the shale taken from the from Foordcoal seams in Stellarton (a town located in Nova Scotia, Canada) was characterized using X-ray diffractometer in the lab of materials engineering department of Dalhousie University. Although shale can contain wide variety of minerals but only three minerals were found in this sample after performing my experiments in the lab which are Illite, Kaolinite and Quartz, in which illite and kaolinite are “Clay Mineral” and quartz is “Non Clay Mineral”. XRD generated fingerprint (set of peaks) for the material. Mineral identification was done by comparison of the experimental pattern with a database of known patterns. It is performed either visually or by using automatic searches but generally a combination of both is used. By converting diffraction peaks into d-spacing, one can identify and tell about the presence of different minerals in a sample.
## LIST OF ABBREVIATIONS USED

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<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>FWB</td>
<td>Fort Worth Basin</td>
</tr>
<tr>
<td>ICDD</td>
<td>International Centre for Diffraction Data</td>
</tr>
<tr>
<td>ICSD</td>
<td>Inorganic Crystal Structure Database</td>
</tr>
<tr>
<td>mD</td>
<td>Milli Darcy</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Micro-image</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Content</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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ACKNOWLEDGEMENT

All praises are for The Almighty, the most Beneficial and the most Merciful.

I would like to extend my gratitude to Dr. Michael. J. Pegg who supervised my work and guided me throughout my degree program. I am also thankful to AdangoMiadonye who added his comments and corrected me where required.
CHAPTER 1

INTRODUCTION TO SHALE GAS (UNCONVENTIONAL RESERVOIR)

1.1 Introduction

The production of natural gas from conventional reservoirs is declining in whole of the world and it is estimated that the production will decline with passage of time like in Canada, United states etc. Now the industry is focusing on the unconventional resources to produce natural gas (i.e. natural gas that can be produced from the low permeability reservoirs like shale or coals). Development of unconventional resources is technically challenging in the coming future.

**Figure 1** shows the location of most important Canadian shale gas plays which are the Horn River Basin and Montneyshales in northeast British Columbia, the Colorado Group of Alberta and Saskatchewan, the Utica Shale of Quebec and the Windsor Group of Nova Scotia.

![Shale Gas in Canada](image)

**Figure 1- Canada shale gas (National Energy Board, 2009)**
1.2 Shale

Shale is the most abundant sedimentary rock. Shale is a rock composed mainly of clay-size mineral grains and is also called a mud rock. It is a sedimentary rock that is usually formed from the compaction of at least 50% silt and clay size particles. That is why shales are also known as mudstones. In reality shale is combination of clay minerals (illite, kaolinite) and non clay minerals such as silica (quartz) and carbonate (calcite or dolomite). It can also contain organic materials, iron oxide and heavy mineral grains. The rock is made up of very thin layers and has thin beds of either sandstone or limestone. Shales are targeted as potential gas reservoirs. The quality of shale reservoirs depends on their thickness and extent, organic content, thermal maturity, depth and pressure, fluid saturations, and permeability, among other factors. Shale can be source, reservoir, and seal for natural gas. It has very low permeability and if we want to take the production economically, then we need advanced method and stimulation techniques.

1.3 Minerals in Shales

Shales can contain a wide range of minerals, although only the clay minerals (Illite, Kaolinite) and non clay minerals (Quartz) were found in my sample of shale by X-ray diffraction. The sample of shale was taken from Foord coal seams in Stellarton, Nova Scotia. Clays have a structure consisting of alternate layers of silica and tetrahedral alumina with a layer of exchangeable cations. The type of clay found in shale is a function of rock type and climate. Depositional environment was once thought to exert a considerable influence on clay mineralogy but it is now known that alteration of the clay framework does not occur, although there is a change in the exchangeable cation population (Russell, 1970). Rock type also plays its part in
clay mineralogy. Illites probably derive from weathering of preexisting illites and chlorites from preexisting chlorites, thus certain rock type generate particular mineralogies.

1.3.1 Illite

Illite is by far the most abundant clay mineral in shale. Illite is a non expanding clay sized alumino-silicate mineral and its structure is constituted by the repetition of tetrahedron-octahedron-tetrahedron (TOT) layers. It seems to be largely derived from preexisting shales and is also the principal clay mineral found in deeply buried shales, where it is associated with the chlorites. There are two structural types of illite known as 1M and 2M. The chemical formula of illite is given as (K,H₃O)Al₂Si₃AlO₁₀(OH)₂. Muscovite is the end product of illite and is believed to be produced with increasing temperature. A special variety of illite is an iron rich mineral known as glauconite. It seems to be exclusively marine and forms during slow sedimentation.

1.3.2 Kaolinite

Kaolinite forms in soils developed under abundant rainfall, good drainage and acid waters. It is a characteristic of tropical and subtropical weathering. In marine basins, it is usually found near shore and is a good indicator of geology in the most ancient of basins. It is a clay mineral with the chemical composition Al₂Si₂O₅(OH)₄. Deer et al., (1992) defined kaolinite as a layered silicate mineral with one tetrahedral sheet linked through oxygen atoms to one sheet of alumina. Kaolinite is a soft and most often white mineral produced by the chemical weathering of aluminium silicate minerals like feldspar. Iron oxide gives it a pink, red and orange color.
1.3.3 Quartz

Quartz forms 20%-30% of the average shale and is almost always present. It is the most common mineral on earth’s surface and is a significant component of many igneous, metamorphic and sedimentary rocks. Quartz belongs to the trigonal crystal system. The ideal crystal shape is a six ended prism with six sided pyramids at each end. It is made up of a continuous framework of SiO$_4$ silicon–oxygen tetrahedra with oxygen being shared between two tetrahedra giving an overall formula SiO$_2$.

1.4 Average Shale Mineralogy

Table 1 shows the average percentage of different minerals in shale.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>58</td>
</tr>
<tr>
<td>Quartz</td>
<td>28</td>
</tr>
<tr>
<td>Feldspar</td>
<td>6</td>
</tr>
<tr>
<td>Carbonates</td>
<td>5</td>
</tr>
<tr>
<td>Iron Oxide</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 1- Average Shale Mineralogy(Pettijohn,1975)

1.5 Types of Shale

Black organic shales are the most common shales found in the earth. They can serve as a source rock for many oil and gas deposits. From the tiny particles of organic matter that were deposited
with mud to form shales, these black shales obtained their black color. The mud was buried and warmed due to the high temperature within the earth and some of the organic material was transformed into oil and natural gas. Just one or two percent organic materials can give black or grey color to the rock. This black color always shows that the sediment, from which shale has formed, was deposited in an oxygen-deficient environment. If any oxygen was entered, it quickly reacted with organic material. An oxygen poor environment also provides the ideal conditions for the formation of sulfide minerals such as pyrite. Gray shales are the rocks that contain calcareous materials or simply clay minerals that result in a gray color. Shales which are deposited in oxygen-rich environments often contain tiny particles of iron oxide or iron hydroxide minerals such as hematite, goethite or limonite. Tomlinson (1916) said that the presence of hematite can produce red shale while the presence of limonite or goethite can produce yellow or brown shale. High ratios of \( \frac{Fe^{3+}}{Fe^{2+}} \) are associated with red colors and low with yellow or brown. Because the \( \frac{Fe^{3+}}{Fe^{2+}} \) ratio is controlled by the oxidation state which in turn is controlled by the amount of organic matter in sediments, all color in shales is ultimately controlled by the amount of organic matter present.

1.6 Shale Gas

Shale Gas is a natural gas that is produced from reservoir which is composed of shale (a fine-grained sedimentary rock which is easily breakable into thin layers), rather than from more conventional sandstone or limestone reservoirs. Shale has low matrix permeability, so in order to take production in commercial quantities from this type of reservoir one has to do fracturing to increase the permeability. Shale gas can be associated with tight gas and coal bed methane. Shales are the source rocks that have not released all of their generated hydrocarbons. Source
rocks that are tight can be the best candidate in forming shale gas potentials. According to [Loucks et al., 2010] shale gas is generated by

- Primary thermogenic degradation of organic matter
- Secondary thermogenic cracking of oil
- Biogenic degradation of organic matter.

The shale gas can be both source rock and the reservoir rock. It has very low permeability. It stores the natural gas by four different ways ([Ruppel et al., 2008])

- Adsorbed onto insoluble organic matter called kerogen
- Trapped in the pore spaces of the fine-grained sediments interbedded with the shale
- Confined in fractures within the shale itself
- Pore network within the organic matter or kerogen

**Figure 2** shows field emission scanning electron photomicrograph of nanoscale pore architecture in the Barnett formation.

![Nanoscale Pore Architecture](image_url)

**Figure 2- Field emission scanning electron photomicrograph of nanoscale pore architecture in the Barnett formation (Reed et al., 2007)**
The free gas resides in fractures and pores in shale and is easier to produce relative to the gas adsorbed. That is why the initial rates of production are higher in shale. They decline rapidly to a low steady rate within about one year as adsorbed gas is slowly released from the shale.

1.7 Tight Natural Gas

Tight natural gas is a gas which is trapped in unusually impermeable hard rock, stuck in a very tight formation underground like sandstone or limestone formation that is impermeable and non-porous (tight sand). Once the conventional natural gas reservoir is drilled, gas can be easily and readily produced but in tight gas sand a great effort has to be put for this extraction. Several techniques including fracturing and stimulation are used in order to take production from this kind of reservoir.

The difference between tight gas sands and shale gas can be explained by this way:

- **In tight gas sands**, grains of sands are tightly cemented together which leads to low permeability and pore throat apertures. As a result, production rates are very small. Content of shale within tight gas sands can be very small. The permeability of tight gas sands is less than 0.1 mD.

- **In shale gas**, the gas is always stored in shale layers. Part of the gas is stored as free gas in fractures, pores within the rock and pores within the organic matter and a part of the gas is adsorbed in kerogen. The permeability of shale gas is in nano-Darcy.

**Naik (2003)** defined **unconventional gas** as a natural gas that cannot be produced at economic flow rates or in economic volumes unless the well is stimulated by a large hydraulic fracture treatment, a horizontal wellbore, or by using multilateral wellbores or some other technique to expose more of the reservoir to the wellbore.
1.8 Conventional and Unconventional Reservoirs

Conventional reservoirs are those reservoirs that can be produce at economic flow rates and by which we can get economic volume of oil and gas. Reservoir fluid can be produce without any special recovery method like stimulation job. Conventional reservoirs have more permeability than that of unconventional reservoir (Naik, 2003).

On the other hand, an unconventional reservoir is the one that cannot be produced at economic flow rates or that does not produce economic volumes of oil and gas unless stimulation treatments or special recovery processes and technologies are used.

Types of unconventional reservoirs are

- **Tight gas reservoirs**
- **Coal-bed methane**
- **Heavy oil**
- **Shale gas**

The unconventional reservoirs need advanced technology if we want to take production from them in the future. Outside of United States, unconventional reservoirs are unnoticed and understudied. Almost in whole of the world, natural gas industry was focusing on the conventional reservoir source but now to compensate the increasing demand of gas, these gas industries have started to pay attention on unconventional gas reservoirs (tight sands, coal bed methane, and gas shales). During past several decades for the development of these unconventional reservoirs, research and new technologies are being used. By using the new technologies in United States, we get 30% natural gas production from the tight sands for domestic gas supply and >25% of daily Canadian oil is recovered from heavy oil sands. Consequently, only limited development has taken place outside of North America.
Now our demand of natural gas has increased. We have to get more and more production from the shale rock. The development of these unconventional gas reservoirs has occurred in Canada, Australia, Mexico, Venezuela, Argentina, Indonesia, China, Russia, Egypt, and Saudi Arabia but with the current technology, it is not possible to take an economical production. Now is the time to find some new technologies to explore these resources. The table given below demonstrates that the estimated volumes of gas in place in coal bed methane, shale gas, tight gas (Tcf). Table 2 shows the summarized work of Rogner (1996) who estimated the worldwide unconventional gas resource.

<table>
<thead>
<tr>
<th>Region</th>
<th>Coalbed Methane (Tcf)</th>
<th>Shale Gas (Tcf)</th>
<th>Tight Gas Sand (Tcf)</th>
<th>Total (Tcf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America</td>
<td>3,017</td>
<td>3,842</td>
<td>1,371</td>
<td>8,228</td>
</tr>
<tr>
<td>Latin America</td>
<td>39</td>
<td>2,117</td>
<td>1,293</td>
<td>3,448</td>
</tr>
<tr>
<td>Western Europe</td>
<td>157</td>
<td>510</td>
<td>253</td>
<td>1,019</td>
</tr>
<tr>
<td>Central and Eastern Europe</td>
<td>118</td>
<td>39</td>
<td>78</td>
<td>235</td>
</tr>
<tr>
<td>Former Soviet Union</td>
<td>3,957</td>
<td>627</td>
<td>901</td>
<td>5,485</td>
</tr>
<tr>
<td>Middle East and North Africa</td>
<td>0</td>
<td>2,548</td>
<td>823</td>
<td>3,370</td>
</tr>
<tr>
<td>Sub-Saharan Africa</td>
<td>39</td>
<td>274</td>
<td>784</td>
<td>1,097</td>
</tr>
<tr>
<td>Centrally planned Asia and China</td>
<td>1,215</td>
<td>3,528</td>
<td>353</td>
<td>5,094</td>
</tr>
<tr>
<td>Pacific (Organization for Economic Co-operation and Development)</td>
<td>470</td>
<td>2,313</td>
<td>705</td>
<td>3,487</td>
</tr>
<tr>
<td>Other Asia Pacific</td>
<td>0</td>
<td>314</td>
<td>549</td>
<td>862</td>
</tr>
<tr>
<td>South Asia</td>
<td>39</td>
<td>0</td>
<td>196</td>
<td>235</td>
</tr>
<tr>
<td>World</td>
<td>9,051</td>
<td>16,112</td>
<td>7,406</td>
<td>32,560</td>
</tr>
</tbody>
</table>

Table 2- Distribution of worldwide unconventional gas reservoirs (Rogner, 1996)
Unconventional reservoirs have very low permeability (less than 0.1 mD) and primarily produce dry gas. We get large volume of gas through these reservoirs. There are several reservoir rocks whose permeability is less but still we are getting economic volume of gas through these reservoirs e.g. sandstone, low-permeability carbonates, shales, and coal bed methane.

Holditch (2006) stated that a vertical well drilled and completed in a tight gas reservoir must be successfully stimulated to produce at commercial gas-flow rates and produce commercial gas volumes. Normally, a large hydraulic-fracture treatment is required to produce gas economically. In some naturally fractured tight gas reservoirs, horizontal wells can be drilled, but these wells also need to be stimulated.

To optimize development of a tight gas reservoir, a team of geoscientists and engineers must optimize the number and locations of wells to be drilled, as well as the drilling and completion procedures for each well. Often, more data and more engineering manpower are required to understand and develop tight gas reservoirs than are required for higher-permeability conventional reservoirs. On an individual-well basis, a well in a tight gas reservoir will produce less gas over a longer period of time than one expects from a well completed in a higher-permeability conventional reservoir. As such, many more wells (closer well spacing) must be drilled in a tight gas reservoir to recover a large percentage of the original gas in place compared with a conventional reservoir.

1.9 Tight Gas Reservoirs

Tight gas reservoirs are those reservoirs containing natural gas and having permeability less than 0.1 mD. Tight gas reservoir is often sandstone or carbonate gas bearing formation. Some
researches have shown its average effective gas permeability to be less than 0.6 mD. Many ultra tight gas reservoirs can have permeability down to 0.001 mD.

Figure 3 shows thin section of a conventional sandstone reservoir that has been injected with blue epoxy. The blue areas are pore space and would contain natural gas in a producing gas field. The pore space is interconnected so gas can flow easily from the rock.

![Conventional sandstone](image)

**Figure 3- Conventional sandstone(Naik, 2003)**

Figure 4 shows thin section of tight gas sandstone. The blue areas are pores. The pores are irregularly distributed through the reservoir and the porosity of the rock can be seen much less than the conventional reservoir.
In conventional sandstone, we can see that pores are connected and gas can flow through the rock where as in tight gas sandstone, pores are irregularly distributed and poorly connected in the formation. We need special methods to produce this gas.

1.10 The Resource Triangle

The concept of the resource triangle was first used by Masters (1979). Figure 5 illustrates the principle of resource triangle. The concept is that all natural resources are distributed log normally in nature. If we take a look on this triangle, then we can see that conventional reservoirs are in less quantity than unconventional reservoirs. The conventional reservoirs are small in size and easier to extract.

As you go deeper into gas resource triangle, you will find lower grade reservoirs which means that permeability is decreasing. However, these low permeability reservoirs (unconventional
reservoirs) are usually larger in size than the higher permeability reservoirs (conventional reservoirs). The main aspect of low quality and low permeability reservoirs is that if we want to produce them economically, then we need improved technology and adequate gas prices. The concept of the resource triangle applies to every hydrocarbon-producing basin in the world. One should be able to estimate volumes of oil and gas trapped in low-quality reservoirs in a specific basin by knowing volumes of oil and gas that exist in the higher-quality reservoirs (Naik, 2003).

Figure 5 – The resource triangle for conventional and unconventional reservoirs (Masters, 1979)
CHAPTER 2
PORE NETWORKS AND FLUID FLOW IN GAS SHALES

2.1 Introduction

The pore networks, reservoir quality, and mechanisms of fluid flow in gas shales are different from conventional reservoirs. The knowledge of shale gas is complex and challenging and still it is not well understood because shale has fine grain particles. Gas permeability in organic matter which is considerably higher than the permeability of non-organic matrix tends to increase the gas permeability in gas shale because of high porosity, single phase flow and gas slippage effect. When connected to natural and hydraulic fractures, the pore network in the organic matter can be the pathway to high gas production in gas shale.

Four types of porous media are present in the gas shale: **Nonorganic matrix, organic matter, natural fracture, and hydraulic fractures.** Organic matters are those matters, which adsorb free gas as well as store free gas, and we know that shale has significant amount of free gas which is stored in the organic matter. The role of organic matter is poorly understood. By image technology and by advanced sample preparation, Reed et al., (2007) said that organic matter, which is present in the Barnett shale, has pores size ranging from 5 to 1000nm. The purpose of this chapter is to examine the potential effects of organic matter on

- Pore types
- Pore networks and permeability
- Fluid flow mechanisms
Figure 6 shows the pore space in conventional sandstone and gas shale.

![Figure 6 – Pore space in sandstone and shale (Reed et al., 2007)](image)

2.2 Pore Types

Curtis (2002) said that gas shale systems have porosity values between 2% to 15%. Gas shale has four types of the porous media: **nonorganic matter, organic matter, natural fractures, and hydraulically induced fracture**. The shale matrix consists primarily of clay minerals, quartz and organic matter. Nano-scale pores and micro-scale pores are two types of matrix pores. Reed et al., (2007) reported nano-scale pores in organic matter and clay rich mud rock. Bustin et al., (2008) reported that micro-scale pores are present mostly in silica rich mud rock.
2.3 Organic Matter

Pore spaces in organic matter range from 5 to 1000 nm and are thought to have generated as oil and gas were formed. Reed et al., (2007) have estimated porosity in organic matter from 0 to 25%. Organic substances are considered to be the media in which hydrocarbons travelled in source rocks. Hydrocarbons can flow either along the surfaces or through organic substances. It shows that these substances are porous media. Figure 7 shows organic matter by SEM (scanning electron micro-image).

![Figure 7 – Scanning electron micro image showing pores in organic matter from the T.P. Sims#2 well, Barnett Shale, FWB (Reed et al., 2007)](image)

Figure 8 shows that adsorbed gas, free gas stored in the matrix, increases linearly with total organic content (TOC). At zero TOC, Figure 8 reflects free gas stored in the nonorganic matrix.
Free gas is stored in the organic matter and can flow through the organic matter. Leveron (1954) suggested that hydrocarbon could flow along the surfaces of organic matter or through the organic matter. It means that organic matter is porous media. Therefore, if gas or oil flows through the organic matter and is predominately single-phase without residual water and gas, permeability is estimated to be high in the organic matter due to Klinkenberg slippage effect (Klinkenberg, 1941). The porosity of organic matter is five times higher than the nonorganic matter.

2.4 Pore Volume Estimation

The pore volume of organic matter is function of porosity and TOC. The TOC is measured in weight% and have to convert into the volume%. As I discussed before that Reed et
al., (2007) reported that the porosity of organic matter is 0 to 25% in the Barnett shale, North Texas. Nelson (1991) assumed the porosity of natural and hydraulic fracture, which is <0.5% & <0.2% respectively. Pore volume in organic matter can be equal to or greater than those in natural or hydraulic fractures. During hydraulic fracturing, the boundaries between organic and non-organic matrix can provide a path for gas to flow. This hidden pore network can play an important role in higher than expected gas production from shales.

Table 3 shows total porosity and TOC values for Barnett Shale in FWB, Marcellus Shale in Appalachian Basin and Hayneville Shale in Louisiana. Estimated porosities in organic matter are 1%, 1.2% and 0.7% of the bulk volume. Hayneville shale is dominated by pores nonorganic matrix more than Barnett and Marcellus Shales. These values increase with the assumed porosity in organic matter.

<table>
<thead>
<tr>
<th>Item</th>
<th>Barnett Shale, FWB</th>
<th>Marcellus Shale</th>
<th>Hayneville Shale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total porosity of shale</td>
<td>5%</td>
<td>6.5%</td>
<td>12%</td>
</tr>
<tr>
<td>Assumed porosity in natural fractures</td>
<td>&lt;0.5%</td>
<td>&lt;0.5%</td>
<td>&lt;0.5%</td>
</tr>
<tr>
<td>Assumed porosity in hydraulic fractures</td>
<td>&lt;0.2%</td>
<td>&lt;0.2</td>
<td>&lt;0.2%</td>
</tr>
<tr>
<td>Total organic content (TOC)</td>
<td>10% (5 wt%)</td>
<td>12% (6 wt%)</td>
<td>7% (3.5 wt%)</td>
</tr>
<tr>
<td>Assumed porosity in organic matter</td>
<td>10%</td>
<td>10%</td>
<td>10%</td>
</tr>
<tr>
<td>Porosity of organics in shale</td>
<td>1%</td>
<td>1.2%</td>
<td>0.7%</td>
</tr>
<tr>
<td>Porosity in nonorganic rock matrix</td>
<td>&gt;3.3%</td>
<td>&gt;4.6</td>
<td>&gt;10.6%</td>
</tr>
</tbody>
</table>

Table 3 – Estimation of pore volume in organic matter (Nelson, 1991)
2.5 Permeability

The permeability of mudrocks is very low (0.1 mD) and measured in subnanodarcy to microarrays. Soeder et al.,(1988) reported that the permeability is the function of shale type, sample type, porosity, confining pressure, and pore pressure.

Two types of sample are used here: core plug, crushed sample. The permeability values measured in core plugs (green squares) are higher than using crushed samples (red circles). Because pore networks in organic matter are connected through micro fractures, the connectivity of organic pore network is reduced in crushed samples (see Figure 9).

![Figure 9 – Porosity and permeability relationships of shale gas plays in North America using core plugs and crushed samples (Soeder, 1988)](image)

Soeder (1988) showed that permeability in the Marcellus shale is pressure dependent and decrease with increase in confining pressure. The effect of confining pressure is caused by
reduction in porosity. **Bustin et al., (2008)** reported the effect of effective stress or confining pressure in Barnett, Muskwa, Ohio, and Woodford shales. **Figure 10** indicates that permeability in shale is greatly reduced with respect to confining pressure than in consolidated sandstone or carbonates. The shale gas permeability should be measured at a confining pressure close to lithostatic pressure at reservoir depth.

![Figure 10 – Effect of confining pressure on gas permeability in gas shales (Bustin et al., 2008)](image)

2.6 **Production Fairways**

Shale has less permeability and it has nanopores because it has fine gained particles. The organic flakes are intersected by the natural fractures. Gas shale can have high permeability network when nanopores in the organic matter are connected with natural micro- and macro-fractures by hydraulic fracturing (**Wang, 2008**). We need a stimulation technique or any advanced technology technique by which we get more production from the reservoir. At the start, there is high gas
production and at the end, it shows low gas production. It means that at the end shale gas is poorly connected with organic matter. The gas rate depends upon (1) the ratio of porosity in the organic matter to the total porosity, permeability, geometry, distribution, and connectivity of organic flakes (2) How organic matter is connected to natural and hydraulic fracture. Figure 11 shows high permeability elements in gas shale.

![Diagram showing high permeability elements in gas shale.](image)

**Figure 11** – Schematic diagram showing high permeability elements in gas shale. (Wang, 2008)

### 2.7 Fluid Flow Mechanisms

Fluid flow through the gas shale is controlled by the flow mechanisms which are

- Free gas flow
- Desorption
- Diffusion
- Imbibition suction
Free gas which flows through the organic and nonorganic matrices is non-Darcy type but it is a Darcy type in natural and hydraulic fractures. Free gas flows through organic and nonorganic matrices due to the slippage effect.

As we know that gas is adsorbed on the organic matter. Due to this, a layer of adsorbed gas increases drag on the gas molecules and causes adverse effect on the permeability. If the organic matter is not a porous media, adsorbed gas is not released from the matrices pores or micro-fractures, and adsorbed gases moved from organic surfaces of pores or fractures only by diffusion. On the other hand, if the organic matter is porous media, therefore, a part of adsorbed gas is released directly into the organic pores and due to this role of diffusion is reduced. Imbibition mostly occurs in the frac water flow in tight gas sandstones (Bennian and Thomas, 2005). In some shales, less than 50% of frac water flows back during production. Combined effects of gravity segregation in fractures and imbibition suction can cause this situation. Gas flows through the upper parts of fractures during production leaving behind water in the lower parts of fracture. Some water can enter into the shale formation during drilling and stimulation and part of it can become residual water in the non-organic matrix and can increase the residual water saturation which can further enhance the effect of imbibition.

When we take the production from the shale gas wells, water production is one of the critical factors which will affect the success of the shale gas wells. If the shale gas is from high-quality shale gas well, then it should have high initial gas saturation and less initial water saturation. Boyer et al., (2006) said that initial water saturation should be less than 30%. Bennion and Thommas (2005) said that this low initial water saturation is sub-irreducible. It has two important affects on the fluid flow through the gas shale during drilling and hydraulic fracturing (1) preventing water from producing (2) creating powerful capillary suction of water.
3.1 Introduction

The term mudrock is referred as fine-grained sedimentary rocks. The range of particle size in the mudrock is less than 0.0625mm. It means that the pores are very small which are at scale of nanometers. The following are the types of the mudrocks.

- **Siltstone** (with 50\% or more silt-size material)
- **Clay stone** (with 50\% or more clay-size material)
- **Mudstone** (hardened mud; it is a mixture of silt and clay sized particles)

Mudstone includes:
- **Shale** (any mudrock that exhibits lamination or fissility or both)
- **Argillite** (has undergone low grade metamorphism)

Generally, mudrocks have fine-grained sediments (<62.5 micrometer). Mudrock which shows fissility (tendency of the mudrock to split along thin closely spaced parallel surfaces) is classified as shales (Blatt et al., 1996) and the mudrock which shows no fissility is classified as mudstones (see Figure 12).
Mudrocks have nanopores and nanogrooves and it is detected by atomic force microscopy (AFM). Now we are confident that these small pores exist in the mudrocks in addition to gas flow into these small pores. Gas flow cannot be described by the Darcy equation because of processes such as Knudsen diffusion and slip flow. These processes separate gas flow from Darcy type flow. Darcy equation was developed for the Darcy flow and it is for the porous media, which has larger pore size than that of nanopores. Nevertheless, the equation that is developed for the nanopores, it includes complexity of the gas flow into the nanopores. We are introducing the term apparent permeability instead of Darcy permeability because of nanopores.

At the equilibrium, gas molecules are dispersed all over the strata. If you see Figure 13, then you can get an idea that gas molecules occupy pores as a compressed gas and cover the surface of the kerogen material as an adsorbed gas (Absorption refers to the process of the penetration of one
material into another whereas adsorption refers to the action of one material being collected on another's surface) and finally disperse in the kerogen material as Dissolve gas.

When we start drilling a well or any activity like hydraulic fracturing, it disturbs the equilibrium and gas molecules start to flow towards the low pressure zone. Javadpour et al., (2007) said that if the pore size is smaller than 100nm, then the ratio between the apparent permeability to Darcy permeability is increased and it means that Knudsen diffusion’s contribution increases. Darcy permeability is attribute of the rock only. However, gas flows into the nanopores of mudrocks depends on the rock type, gas type, and operating conditions.

3.2 Detection of Nanopores and Nanogrooves by Atomic Force Microscopy (AFM)

Mudrocks have fine-grained particles. If we want to see the size of these small pores, then we need a device which observes the size of these fine-grained particles. AFM is used in the
biological systems and by this; we can directly measure the topography of the surfaces to study the geometry of the pore network at nano and micro-scale (Magonov and Whangbo, 1996). The AFM is used to measure the surface forces directly like Vander walls and electrostatic forces between the molecule of interest and minerals in the rock.

From the AFM, we can detect pores as small as 5nm. You can see in the Figure 14 that few pores whose size range is 30nm and nanogroove with a width of 60nm was detected. The AFM study proved that these small pores exist in these mud rock systems.

Figure 14 – AFM image of nanopores and nanogrooves in mud rock (Magonov and Whangbo, 1996)

3.3 Macroscopic Gas Flow in Porous Media

Bird (2007) gave mass conservation equation for a fluid flowing through a network of pores as

$$\frac{\partial p}{\partial t} = - (\nabla \cdot \rho u)$$

………………………………………………3.1
In the range of tens to hundreds of microns, Darcy’s law can be assumed for the velocity term as

\[ u = -\frac{k}{\mu} (\nabla p) \]  \hspace{1cm} \text{(3.2)}

Substituting equation (3.2) into (3.1),

\[ \frac{\partial p}{\partial t} = - \left[ \nabla \cdot \rho \left( \frac{k}{\mu} \nabla p \right) \right] \]  \hspace{1cm} \text{(3.3)}

Where,

\( k \) = absolute Darcy permeability, \( m^2 \)

\( \mu \) = fluid viscosity, \( \text{Pa.s} \)

\( p \) = pressure, \( \text{kPa} \)

\( t \) = time, \( \text{s} \)

\( \rho \) = density, \( \text{kg/m}^3 \)

When the pores are in the range of tens to hundreds of microns, then we will use the flow equation (3.3) for a compressible fluid flowing in the porous media. This equation is for the conventional reservoirs but our system of interest is mudrock having nanopores where Darcy permeability is not valid.

### 3.4 Gas Flow in Nanopores

Total mass flux of a gas through a nanopore is combination of Knudsen diffusion and pressure forces and is termed as \( \mathbf{J} \)

\[ \mathbf{J} = \mathbf{J_a} + \mathbf{J_D} \]  \hspace{1cm} \text{(3.4)}

Where,
\( \bar{J} = \text{Total mass flux, kg/s/m}^2 \)

\( \bar{J}_a = \text{Advective flow due to pressure forces} \)

\( \bar{J}_D = \text{Knudsen diffusion (Javadpour et al, 2007)} \)

### 3.5 Model Results

In this section, analyses with different parameters such as pore size, pressure, temperature and gas molar mass on apparent permeability of mudrock are presented.

#### 3.5.1 \( K_{\text{app}}/K_D \) ratio vs Pore Size

**Figure 15** shows the \( k_{\text{app}}/k_D \) ratio of the porous media of different pores sizes. The \( k_{\text{app}}/k_D \) is higher when pore size is smaller. There is no difference between the apparent and Darcy permeability when pores have size range of 1 micrometer.

![Figure 15 – \( k_{\text{app}}/k_D \) as a function of average pore radius size (Javadpour et al., 2007)](image-url)
3.5.2 Contribution of Knudsen Diffusion to Total Flux

Knudsen diffusion contribution is not included in the flow models if we are dealing with the conventional system. We can see from Figure 16 that wherever we have small pores, Knudsen diffusion is higher but if the pore sizes are higher than 100 micrometer, the contribution by Knudsen diffusion is negligible.

It means that if we have larger pore size, then Knudsen diffusion contribution to diffusion flux (amount of substance that will flow through a small area during a small time) does not play any part in the flow model but if we keep on decreasing pore size, then Knudsen diffusion contribution increases.

![Figure 16 – Contribution of Knudsen diffusion in total flux vs pore size (Javadpour et al., 2007)](image)

3.5.3 Effects of Pressure and Temperature

Figure 17 demonstrates the effect of pressure and temperature on $k_{app}$: $k_D$ ratio. The temperature has the lowest effect on the $k_{app}$: $k_D$ ratio where as $k_{app}$: $k_D$ ratio is sensitive to the pressure. If the pressure is low, then $k_{app}$: $k_D$ ratio is more because mean free path of the gas molecules increases.
We can observe the effects of pressure and temperature on the contribution of Knudsen diffusion to the total flux. Figure 18 shows that at lower temperature and pressure, diffusion flux contribution is higher whereas at higher temperature and pressure, diffusion flux contribution is lower.
3.5.4 Effect of Gas Molar Mass

Figure 19 shows that gas molar mass has a minimal effect on the $k_{app} : k_D$ ratio with a small increase at lower molar mass values.

![Figure 19–Effect of molar mass on $k_{app} : k_D$ ratio (Javadpour et al., 2007)](image)

On the other hand, Figure 20 shows that diffusion flux coefficient is higher if the molar mass of gas is higher at the same pressure, temperature and pore size. This is because molar mass changes both diffusion flux and slip coefficient.

![Figure 20 – Effects of molar mass on diffusion (Javadpour et al., 2007)](image)
CHAPTER 4

X-RAY DIFFRACTION

4.1 Introduction

X-ray diffraction (XRD) is a basic tool in the mineralogical analysis of shales. It is an analytical technique primarily used on a crystalline material to identify its phase and can provide information on unit cell dimensions. It is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). From a small area, XRD measures the intensities of a reflected area and from the results obtained; atomic-level spacing of the crystal can be calculated. This helps in understanding the crystal structure for the substance. Determination of the degree of crystallization can also be calculated with the help of XRD. Furthermore, XRD also helps in identifying different phases with identical compositions such as the state of atomic order. Due to this versatility, XRD finds wide range of applications in geology, material science and environmental science. **Figure 21** shows the schematic diagram of X-ray diffraction pattern.

![Schematic diagram X-ray diffraction pattern](image)

**Figure 21 – Schematic diagram X-ray diffraction pattern (Gowariker et al., 1986)**
4.2 X-ray Generation and Properties

X-rays are electromagnetic high energy and high frequency radiations. For diffraction applications, only short wavelength X-rays are used because the wavelength of X-rays is comparable to the size of atoms. They are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic (hard) X-rays can penetrate deep into the materials and provide information about the bulk structure (Holman and Benedict, 1996).

Generally, X-rays are produced in the cathode ray tube where filament is heated and by the heating of the filament, high-speed electrons are produced that collides with the target metal (Whaites et al., 2002). These produced electrons are accelerated towards a target metal by applying a voltage and produces X-rays by impact of high-speed electrons on the target metal. When a free electron fills the shell, an X-ray photon with energy characteristic of the target material is emitted. Common targets used in X-ray tubes include Cu and Co.

4.3 Lattice Planes and Bragg’s Law

When X-rays collide with electrons, some of the rays will be deflected away from the direction in which they were originally travelling. If these scattered X-rays did not lose their energy, their wavelength will remain the same and the process is called elastic scattering (Rayleigh, 1871) which means only the momentum has been transferred in the scattering process. These are the x-rays that we measure in diffraction experiments as they carry information about electron distribution in materials. On the contrary, in the inelastic scattering process X-rays transfer some of their energy to the electrons and the scattered X-rays have different wavelength than the incident X-rays.
The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law (Bragg, 1913)

\[ n\lambda = 2d \sin \theta \]

\( \lambda \) = wavelength of X-ray radiation
\( d \) = inter-planar (lattice) spacing
\( \theta \) = diffraction angle
\( n \) = order of the diffraction peak

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. Constructive interference (when a crest of one wave meets with crest of another wave) is the basis of X-ray diffraction. Diffraction occurs when the wavelength is similar to the distance between the atoms. These diffracted X-rays are then detected, processed and counted. All possible orientations of the sample are present, so scanning through a range of \( \theta \) (2 \( \theta \)) will give all possible situations where the Braggs Law is satisfied.

When incident X-rays are diffracted from a crystalline solid surface and constructive interference happens, then each diffraction will generate a peak in the diffractogram. Conversion of the diffraction peaks into d-spacings (The distance between similar atomic planes in a mineral i.e. the interatomic spacing) allows identification of the mineral because each mineral has a set of unique d-spacings. This is achieved by comparison of d-spacings with standard reference patterns. **Figure 22** shows incident and diffracted X-rays.
4.4 Working of X-ray Diffractometer

The X-ray diffractometer consists of three basic elements

i) An X-ray tube

ii) A sample holder

iii) An X-ray detector

X-rays are produced in a cathode ray tube by heating the filament to produce electrons and accelerating them to the target material by applying a voltage. As the sample and detector are rotated, the intensities of diffracted X-rays are recorded. When Bragg’s equation is satisfied, it means that the geometry of diffracted X-rays shows constructive interference and peak shows up in the diffractogram. The detector, which is present inside the diffractogram, records that intensity. This intensity is then converted into a count rate, which is displayed and recorded into the monitor. The geometry of the diffractometer is such that the sample rotates the X-rays beam

Figure 22 – Incident and diffracted X-rays (Bragg, 1913)
at an angle of $\theta$, whereas X-rays, which are diffracted, rotates an angle of $2\theta$. The goniometer rotates the sample and detector.

### 4.4.1 Strengths of XRD Diffraction

- Rapid and powerful technique for identification of an unknown mineral.
- In most cases, it provides an unambiguous mineral determination.
- Sample preparation required is minimal.
- XRD units are widely available.
- Data interpretation is relatively straightforward.

### 4.4.2 Limitations of XRD Diffraction

- Homogeneous and single phase material is best for identification of an unknown.
- Must have access to a standard reference file of inorganic compounds.
- For mixed materials, detection limit is ~2-5% of sample.
- In mixed samples, identification of all phases can be difficult and time consuming.

### 4.4.3 Applications

**Brady et al., (1995)** gave applications of XRD

- XRD is used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds).
- Characterization of crystalline materials.
- Identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically.
➢ Determination of unit cell dimensions.
➢ Measurement of sample purity.

4.5 Requirements for an Ideal XRD

Reduction of the sample size is one of the chief considerations of the sample preparation. The number of the diffracting particles is inversely related to their size. The sample size should be small enough so that it fits in the sample holder and the surface of the sample should not be rough and irregular. It should be made smooth so that we have better results in our experiment.

4.6 Qualitative Phase Analysis

Each X-ray diffraction pattern has a unique set of Bragg peaks
• Peak positions are defined by the unit cell.
• Peak intensities result from the distribution of atoms present.

Thus, each crystalline material has its own “fingerprint” (set of peaks). This permits x-ray diffraction to be used for phase (mineral) identification. Phase identification is done by comparison of the experimental pattern with a database of known patterns. The Powder Diffraction File of the International Centre for Diffraction Data (ICDD-PDF) contains either or both the experimentally measured and calculated digitized patterns for hundreds of thousands of compounds. It includes minerals, metals and alloys, inorganic materials, organic compounds and pharmaceuticals.

Phase identification is performed either visually or by using automatic searches but generally a combination of both is used. Automatic search/match is rapid, uses multiple Bragg reflections and
searches the database available (many hundred-thousand entries). Critical search/match parameters include:

- The number of Bragg peaks that match in position and in relative intensity (to a lesser extent).

- The tolerance or difference in positions between the observed and database peaks as long as the deviation remains within the tolerance, peaks are considered to match.

Automatic searches usually generate a large number of matches. The correct solution should be selected manually by the user. This may involve simple visual matching, or an understanding of the sample.
CHAPTER 5

LABORATORY EXPERIMENT

5.1 Introduction

Clearly the concept of X-ray diffraction has been explained in the previous chapter. Using the X-ray diffractometer in the laboratory of Materials Engineering, a sample of shale was investigated. The sample of shale was taken from Foord coal seams in Stellarton (a town located in Nova Scotia, Canada). Stellarton owes its name to one of its oil shales which came to be known as stellarite because of the stars of fire given off by its sparky flame. The Foord coal seam runs through most part of the town and is said to be the thickest in the world with estimate of coal seams being as thick as 48 feet. The objective of this experiment is to identify the different minerals present in shale and to find out whether any swelling clays are present or not.

5.2 Experimental Procedure

The surface of the sample was made smooth by rubbing it against a sand paper. Once the surface got smooth, sample was put in the sample holder of the X-ray diffractometer and a test was conducted on it.

Figure 23 shows the X-ray diffractometer with interlocks and shielding. The beam functions only with the doors closed. The glass permits viewing of the instrument, but shields the viewer from X-rays.
5.2.1 Machine Specifications

USER: XRD lab

DATE: Tuesday, July 10, 2012

10 position sample changer- samples were run using a top-pack mount at a speed of 2 degrees 2-theta per minute with a step size of 0.05 degrees.

FILE: [Shale.raw] Shale

SCAN: 5.0/90.0041/0.04991/17.9(sec), Copper tube(40kV,40mA), I(p)=2105.

PEAK: 25(pts)
NOTE: Intensity = Counts, Wavelength to Compute d-Spacing = 1.54059Å (Cu/K-alpha1)

Samples ran from 5 to 90 degrees on continuous scan at 2 degrees 2–theta per minute with a step size of 0.05.

Data interpretation done using EVO.

**EVO** using the 2010 ICDD +2011 ICSD.

### 5.3 Results

The following results were obtained by XRD. XRD was used to identify the clay minerals and other minerals present in the shale rock sample. Clay minerals were identified which typically consists of **Kaolinite, Illite** and non clay mineral such as **Quartz** in the sample. All of these minerals were identified by the fact that each mineral has unique fingerprints.

#### 5.3.1 Mineral Identification of Sample

**Table 4** shows the number of minerals which were found in the sample of shale.

<table>
<thead>
<tr>
<th>2-Theta</th>
<th>d(Å)</th>
<th>Intensity</th>
<th>Intensity%</th>
<th>Phase ID</th>
<th>d(Å)</th>
<th>h</th>
<th>K</th>
<th>l</th>
<th>2-Theta</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.819</td>
<td>10.0187</td>
<td>276</td>
<td>13.5</td>
<td>Illite-2M1</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>8.836</td>
</tr>
<tr>
<td>12.357</td>
<td>7.1573</td>
<td>531</td>
<td>26</td>
<td>Kaolinite-1A</td>
<td>7.1709</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>12.333</td>
</tr>
<tr>
<td>17.749</td>
<td>4.9932</td>
<td>94</td>
<td>4.6</td>
<td>Illite-2M1</td>
<td>5.02</td>
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<td>0</td>
<td>4</td>
<td>17.653</td>
</tr>
<tr>
<td>19.885</td>
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<td>58</td>
<td>2.8</td>
<td>Kaolinite-1A</td>
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<td>2</td>
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<td>19.859</td>
</tr>
<tr>
<td>20.861</td>
<td>4.2549</td>
<td>413</td>
<td>20.2</td>
<td>Quartz</td>
<td>4.255</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>20.86</td>
</tr>
<tr>
<td>24.887</td>
<td>3.5749</td>
<td>347</td>
<td>17</td>
<td>Kaolinite-1A</td>
<td>3.5797</td>
<td>5</td>
<td>0</td>
<td>2</td>
<td>24.852</td>
</tr>
<tr>
<td>26.653</td>
<td>3.3418</td>
<td>2046</td>
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Table 4 – Summary of Mineral Identification of the Sample

5.3.2 Fingerprints of the Sample

The following graph (Figure 24) between intensity (counts) and 2-theta (degree) was obtained which shows different peaks of different minerals in shale.
Figure 24- Fingerprint of Sample
5.3.3 **Fingerprints of Each Mineral in Sample**

**Kaolinite**

Fingerprint of kaolinite is like this (Figure 25)

![Figure 25- Search and Match Analysis for Kaolinite in sample](image)

**Illite**

Fingerprint of illite is like this (Figure 26)
Figure 26- Search and Match Analysis for Illite in sample

Quartz

Fingerprint of quartz is like this (Figure 27)
Combination of All Minerals in Sample

**Figure 28** shows search and match analysis for combination of all the minerals in sample.

![Figure 28- Search and Match Analysis for combination of all minerals in sample](image)

**Note**

The numbers which are written on the lines shows the number of matched peaks of minerals and shale.

### 5.4 Raw Data of Shale Rock Sample

After getting results from the XRD lab, graph **(Figure 29)** is plotted between intensity (counts) vs. 2-theta (degree) which shows different peaks of different minerals.
5.5 Table of Minerals in Sample

Table 5 represents clay minerals (Kaolinite and Illite) and non clay mineral (Quartz) found in the sample.

<table>
<thead>
<tr>
<th>Clay Minerals</th>
<th>Non Clay Mineral</th>
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<td>• Kaolinite</td>
<td>• Quartz</td>
</tr>
<tr>
<td>• Illite</td>
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Table 5- Minerals in Sample
5.6 Discussion

Although shale can contain large amounts of various minerals depending on its burial history and sedimentation, but only clay minerals (**Illite**, **Kaolinite**) and a non clay mineral (**Quartz**) were found in this sample by X-ray diffraction. Usually large quantity of illite indicates older rocks. Achieving success in qualitative analysis of XRD by employing any search/match program becomes increasingly challenging as the complexity of the diffraction pattern increases, especially when a material is a mixture of several phases.

**Table 1** indicates clay mineralogy of shale. It shows that clay minerals and quartz constitute most part of the shale whereas feldspar, carbonates and iron oxide are present in small amounts. **Table 2** shows distribution of worldwide unconventional gas resources which indicates that shale gas has largest number of resources as compared to coal bed methane and tight gas sand.

In **Table 4**, the highest peak in the column Intensity sets the Y axis (intensity) height and then all the other peaks in that column are compared to the highest peak. In the column Intensity, 2046 is the value of the highest peak. This peak is given the value of 100% in the column Intensity% and then all the peaks are measured by comparing them to this peak. Columns of h, k and l values represent set of numbers which are uniquely used to identify the plane or surface. The first columns of 2-theta and d-spacing are referring to the value of the peaks in the sample and the second columns of 2-theta and d-spacing are referring to the values from the ICSD or ICCD card for the mineral matched. Then there is another column called Delta which is the difference between the measured value and the card value of 2-theta.
Figures 30, 31 and 32 shows search and match analysis of Kaolinite, Illite and Quartz. A diffraction pattern records the X-ray intensity as a function of 2-theta angle. These figures show the standard diffraction patterns of these minerals with the diffraction pattern of sample of shale. The peaks are produced in the diffraction pattern only in the case of constructive interference and when X-rays are diffracted from a crystalline surface. In case of destructive interference, areas without peaks are produced on graph of intensity vs 2-theta angle.

Low angles or low peaks indicate that we have large d-spacings. Whenever the distance between the atoms of the material will be greater than the wavelength of incident X-rays, peaks will not be produced. Figure 33 shows the search and match analysis for combination of all minerals in the sample. It shows number of matched peaks between minerals and shale. The diffraction peaks are converted into d-spacings which allows identification of the mineral because each mineral has a set of unique d-spacings. It is done by comparison of d-spacings with standard reference patterns. The height of peaks produced by a certain mineral does not indicate anything about its quantity. It just shows that mineral has a good crystalline form. In this case, quartz produced highest peaks as compared to the other minerals which show it has a better crystalline form.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The following conclusions can be drawn based on the whole of the study of my thesis

1. Shale is the most abundant sedimentary rock and is combinations of wide variety of minerals but only these minerals were found in this sample which is illite, kaolinite and silica (quartz).

2. Shale has low matrix permeability, so in order to take production in commercial quantities from this type of reservoir; we have to do fracturing to increase the permeability.

3. In tight gas sands, grains of sands are tightly cemented together which leads to low permeability whereas in shale gas, the gas is always stored in shale layers.

4. The concept of the resource triangle is that conventional reservoirs are less in quantity than the unconventional reservoirs. As we go deeper into the triangle, permeability decreases and price to extract that resource increases. Conventional reservoirs have more permeability than unconventional reservoirs.

5. Gas shale has four types of porous media: organic matrix, nonorganic matrix, natural fracture, hydraulic fracture. Organic matter pore sizes ranging from 5 to 1000 nm are significantly important because they can absorb gases, as well as store free gas.

6. The porosity of organic matter is five times higher than nonorganic matter. Gas permeability of organic matter is higher than that of nonorganic matter due to high porosity, single phase flow and gas slippage effect.
7. XRD is used for identification of different crystalline materials in the rock formation.

8. Each mineral has its own unique fingerprint.

9. Illite, Kaolinite and Quartz are the minerals present in this sample of shale.

10. Quartz and Illite are usually the most common minerals in shale.

11. Quartz peaks are better or highly diffracted because quartz has good crystalline form. Quartz shows larger peaks. On the other hand, clays does not diffract better because they do not have good crystalline form and consequently, their peaks are lower than of quartz.

12. Peak height of quartz does not tell about the quantity. It means that quartz has good crystalline form. It is difficult to get the quantitative results of the clays. The reason is that they do not have good crystalline form and do not diffract better.

13. The different minerals are identified according to the known patterns present in the standard reference patterns.

14. There are no swelling clays (smectite, bentonite) in the sample.

6.2 Recommendations

The software installed in the laboratory does not have the ability to perform quantitative analysis.

The quantity of different minerals in the sample cannot be calculated with the help of it.

I recommend that advanced software be brought into the laboratory to calculate the quantity of minerals besides identification by X-ray diffraction.
References


