Smectite to Illite Transformation of Gulf of Mexico - Eugene Island (GoM-EI) Mudrock

by

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Predicting pore pressure is an important job in the petroleum industry. Standard methods for estimating pressure do not apply to the basin where overpressure is often observed. Compaction disequilibrium and clay mineral diagenesis are recognized as potential contributors to overpressure generation. My research aims to look at the relationship between smectite-to-illite transformation and overpressure generation.

The proposed research has two phases. Phase one objective is to study the reaction rate and the conditions such as temperature, time, KCl concentration that induce smectite-to-illite transformation. Phase two study objective is to investigate the change in compressibility and permeability of resedimented GoM-EI mudrock due to smectite-to-illite transformation.

This thesis presents the results of phase one study. In phase one study, we have successfully transformed smectite to illite in laboratory environment using GoM-EI as starting material. Based on mineral composition results of cooked samples, it is clearly that illitization goes through three stages. The first stage is that a highly smectitic clay is represented by randomly ordered illite-smectite mixed layer phase (I/S). With increasing reaction, randomly ordered I/S are transformed into regularly interstratified structures. The third stage is that the ordered I/S reacts to a final discrete illite. Additional thermal gravimetric analysis (TGA) study on cooked samples confirms that the transformation is releasing water. However, we are unable to determine the volume change of the sample using mineral study.
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Chapter 1

Introduction

1.1 Problem Statement

The percentage of illite increases with depth in Gulf of Mexico basin due to the conversion of the mineral smectite to illite. The ratio of illite to smectite is indicative of temperature and pressure condition in the basin. This ratio is used for oil reservoir characterization and overpressure prediction. Although there have been numerous studies on the mineralogical aspect of smectite-to-illite transformation, the mechanical effects of the clay transition are not fully understood. The ultimate goal of my research is to study permeability, compressibility and creation of overpressure of mudrocks with different degrees of illitization.

This thesis is the phase one of my Ph.D study and studies the conditions such as temperature, time and KCl concentration that induce smectite-to-illite transformation using Gulf of Mexico-Eugene Island (GoM-EI) mudrock as starting material. The phase one study also develops analytic method to characterize mineral composition for transformed GoM-EI material using x-ray diffraction (XRD).

1.2 Thesis Objectives and Scope

The research presented in this thesis has three main objectives.

The first objective is to develop a equipment to induce the smectite to illite trans-
formation in the laboratory within a time effective period. In nature, this process takes millions of years while the laboratory experiments will use elevated temperatures to cause transformation in weeks.

The second objective is to develop a solid method to analyze clay mineral sample and quantify the smectite and illite mineral percentages.

The third objective of the research is to characterize the temperature effect and time effect on smectite-to-illite transformation using GoM-EI mudrock.

1.3 Organization of Thesis

Chapter 2 provides a background summary of the smectite-to-illite transformation and the geological features of Gulf of Mexico-Eugene Island from where the pretest material was extracted. It presents literature review of the transformation mechanism and hydrothermal reaction done by other researchers.

Chapter 3 is dedicated to provide the general structural features of clay minerals from the assembly of tetrahedral sheet and octahedral sheet to layer stacking order of smectite and illite. Clay minerals were treated as crystalline material to study their atomic structure. This chapter is closely related to Chapter 4 and helps to understand the behaviors of clay mineral in x-ray diffraction.

Chapter 4 describes sample preparation procedures for x-ray diffraction and the computer algorithm that is used to quantify clay mineral composition.

Chapter 5 details the equipment and procedures used in carrying out hydrothermal reaction for GoM-EI. Temperature condition, time, KCl concentration for each test are listed.

Chapter 6 presents the results of mineral composition for hydrothermally reacted GoM-EI material. GoM-EI post-test samples have displayed color change due to smectite-to-illite transformation. Color change provides an estimation of the degree of the illitization. This chapter also covers clay mineral identification of GoM-EI sample by peak position using XRD. The quantitative analysis was done by Dr. Day-Stirrat. Based on mineral composition results of cooked samples, it is clearly that
illitization goes through three stages. The first stage is that a highly smectitic clay is represented by randomly ordered illite-smectite mixed layer phase (I/S). With increasing reaction, randomly ordered I/S are transformed into regularly interstratified structures. The third stage is that the ordered I/S reacts to a final discrete illite.
Chapter 2

Background

In the early 1960s, researchers in the Gulf of Mexico noticed that the illite percentage in the clay fraction increases with depth due to smectite-to-illite transformation (Perry & Hower, 1972). During the transformation, a mixed-layer illite/smectite (I/S) phase is formed. This smectite-to-illite transformation is a result of the thermal history of the basin, chemistry of the pore fluid, the mineral composition of the mudrock, and etc. (Hower et al., 1976).

The transformation has been observed in great detail in shales and sandstone. The ideal temperature at which smectite-to-illite transformation occurs ranges from 80°C to 150°C (Nadeau et al., 1985) at Norwegian continental shelf. Fig. 2-1 presents field data from well A and well B at the Gulf of Mexico. In both wells, at a temperature below around 70 °C, the illite percentage stays constant and is independent of temperature. When the temperature is above a certain threshold, illite percentage starts to increase with temperature. There is no upper temperature for the transformation to stop, but there is an upper limit for illite percentage. The illite percentage does not keep increasing with temperature once it reaches 80%. The 80% is unique to Gulf of Mexico area. At North Sea basin the illite percentage can reach more than 90% in the I/S. Bjorlykke (1998) pointed out that depletion of potassium in the Gulf of Mexico prevents illite growing to 100% in the mixed-layered I/S.

The attention for studying this conversion was drawn for two main reasons: 1. it is important to understand the thermal history of rocks or shales in fossil geothermal
fields; 2. the transformation of smectite is accompanied by a release of interlayer water which could be one of the reasons for overpressure observed in the Gulf of Mexico.

2.1 Overpressure at the Gulf of Mexico

Overpressure or fluid pressure in excess of hydrostatic pressure has been observed in many sedimentary basins. Tectonic stress, rapid deposition of low permeability sediments and clay mineral diagenesis are recognized as potential contributors to overpressure generation. In the petroleum industry, knowledge of the distribution of overpressure is critical in exploration, drilling, and production. Fig. 2-2 shows a generalized pore pressure trend at the Gulf of Mexico. At a depth of 3km-5km, pore pressure quickly ramps up reducing the effective stress. Thus, the safety factor for drilling will decrease dramatically.

There are two main schools of thoughts that explain the generation of overpressure at a sedimentary basin. Studies by Osborne and Swarbrick (1997) and Hart et al. (1995) emphasize that compaction disequilibrium plays a significant role in generating overpressure. Disequilibrium compaction refers to the situation where sediments are unable to expel their pore fluids in response to sediment loading, which causes fluid overpressure. As often the case at the Gulf of Mexico, sediment's permeability is low enough that pore fluids do not escape freely. Pore pressure is built up due to overlaying sediment load and low permeability.

Studies by Lahann (2002) and Bowers (2011) emphasize the connection between clay mineral diagenesis and overpressure. If the density of interlayer water is denser than the pore water (Bowers 2011), when the interlayer water is released to pore, the volume of interlayer water or bound water will expand as the water density drops to 1 g/cm$^3$. So in a closed system, the pore pressure will increase dramatically due to the release of interlayer water. But there is no actual measured data to confirm the theory, this motives the current research to figure out the volume change due to smectite-to-illite transformation and the relationship between overpressure generation
and smectite-to-illite transformation.

2.2 Transformation Mechanism

Numerous researchers have studied smectite to illite transformation. Hower et al. (1976) proposed a layer by layer transformation theory. The surface charge on the clay sheet continues to develop, and finally leads to $K^+$ fixation in the interlayer space of smectite. When the attraction between $K^+$ and negatively charged clay surface overcome the hydration energy of cations, water is released from interlayer space. In consequence, the d-spacing of a unit cell decreases from 15 Å (fully expanded smectite) to 10Å (shown in Fig. 2-3). But the collapse of interlayer space alone does not guarantee the formation of illite, one needs to determine the chemical composition change of the mineral. The real illite needs to reach a minimum number of 0.75 K per O10(OH)2 in the unit chemical formula (Meunier & Velde, 2013).

Lagaly’s research (1986) further explained the selective process of potassium fixation. He pointed out the diameter of $K^+$ fits particularly well to the dimension of the ditrigonal cavity on the tetrahedral sheet, so that $K^+$ acts as a bonding agent between two clay layers.

2.3 Gulf of Mexico -Eugene Island Mudrock

The Gulf of Mexico- Eugene Island(GoM-EI) was retrieved from Eugene Island block located off the coast of Louisiana. The source material used in my research project was extracted from two cores namely A-20ST in Block 330 and A-12 in Block 316 (Fig. 2-4). The cored section was at an elevation below seabed between 6690'(2039m) and 7550'(2301m). The material had been air-dried, roller ground to a fine powder with 99 % passing the #100 sieve, and homogenized. The geological environment in Block 330 was well studied and documented by Losh et al.(1999) and Hart et al.(1995). It was a major scientific endeavor to study and understand the geologic, chemical and thermal conditions of a major growth fault(also termed as A fault in Fig. 2-5.
and Fig. 2-6) and the related oil and gas potential. Fig. 2-5 illustrates the relative borehole location to the fault. A-12ST is located on the upthrown block to the north of the A fault. The cored interval begins below the upper Lentic 1 sand (Alexander & Flemings, 1995), shown in the Fig 2-5 as a stem at the end of the borehole. A-20ST cored intervals penetrated through the fault. They were extracted from the footwall. According to Losh et al. (1999), A-20ST core consists of three structural domains:

1. Domain 1 - calcareous silty mudstone

2. Domain 2 - noncalcareous silty mudstone, clayey silt, laminated to medium-bedded sand

3. Domain 3 - noncalcareous silty mudstone, oil-bearing faults

Besides their structure difference within the cored sections, Losh et al. (1999) looked into mineralogical composition. He summarized the mineralogy of shale samples from whole core and sidewall cores of A-20ST well from 1500 to 2415 m SSTVD (subsea true vertical depth). From the Fig. 2-7 we can see illite/(illite + smectite) ratio increase with depth. Losh found that the ratios are unusually high for Pliocene-Pleistocene sediments at 2.3 km burial depth. Similar high ratios are observed at shallower depth and lower temperature in A-20ST. The reason for high illite content is not totally understood, but it can be possibly explained by high potassium content in the brine. Losh supported his idea with the discovery from Hover et al. (1994) that potassium exchange for sodium in smectite during early diagenesis leads to a potassium-enriched precursor. This K⁺-smectite may transform to illite at a lower temperature.

Hart et al. (1995) described the pore pressure and overburden stress for well A-20ST2. The upper 1500m(4800ft) are hydrostatically pressured, followed by a moderately overpressured transition zone from 1500m(4800ft) to 2000m(6500ft), and then severe overpressures, equaling up to 95% of the total overburden pressure occurring below 2000m(6500ft)(shown in Fig. 2-8). Other wells in the Eugene Island Block 330 field show similar pressure profiles, though the depth at which the overpressure is encountered varies with the basin structure.
2.4 Hydrothermal Tests Using Pure Smectite

Typical reservoir pressure-temperature (P-T) conditions are shown in shaded area of Fig. 2-9. Pressure here is overburden pressure of the reservoir. The geothermal gradient for the Gulf of Mexico is around 21°C/km according to Forrest (2005), so the Gulf of Mexico P-T condition follows the left edge of the shaded area. In nature, the smectite-to-illite transformation takes millions of years. In order to study the mineral transformation in a practical time scale, experimental studies are mostly conducted at elevated temperatures. Rosenberg (1996) conducted his experiments in an autoclave condition where pressure follows the saturated vapor pressure curve for pure water at certain temperature. Small & Manning (1993) and Huang (1993) increased the pressure in their experiments to 50MPa and 100MPa in order to simulate the reservoir pressure.

It is believed that observing a simple system would give insight into reactions in complex systems. Huang conducted a series of hydrothermal reaction tests using pure smectite as his starting material. Each data point in Fig. 2-10 and Fig. 2-11 is the result of one hydrothermal test. The variations in these tests are temperature, run time and KCl concentration.

Based on Huang’s results, the smectite to illite transformation is mostly temperature driven. The reaction rate increases with temperature as shown in Fig. 2-10. The KCl concentration is 1 mol/L for tests plotted in Fig.2-10.

Huang concluded that the chemical composition of the fluids also affect the reaction. With higher $K^+$ concentration, the reaction rate is faster as shown in Fig. 2-11. The temperature is 275 °C for tests plotted in Fig.2-11. Huang also found that extensive amount of $Mg^{2+}$ and $Na^+$ retards reaction.
Figure 2-1: The relation between burial depth, temperature and proportion of illite layers in mixed-layer phase. (Perry and Hower 1972)

Figure 2-2: Generalized Pore Pressure at Gulf of Mexico (Statoil Oil, 2005). The pore pressure follows hydrostatic line for depth below 3km. At a depth from 3-4km, the pore pressure moderately overpressures. At depth higher than 4km, the pore pressure severely overpressures.
Figure 2-3: Structure of Smectite and Illite

Figure 2-4: Location of Block 330 (Losh, 1999). Well A-20ST and well A-12 are labeled on the map.
Figure 2-5: Profile View of Well A-20ST and Well A-12 (Alexander and Flemings, 1995). The GOM-EI sample used in my tests were cored from A-20ST and A-12 wells green enlarged section.
Figure 2-6: Structure Domains of Well A-20ST Cored Section (Losh, 1999)

Figure 2-7: I/ (I+S) % vs. In-situ Temp. (°C) vs. Depth (mbsf)

Illite Ratio of Well A-20ST (Losh, 1999). Samples are from side wall.
Figure 2-8: Well Data of A-20ST (Hart, 1995) Pore pressure data is the third figure, overpressure is recorded at depth of 7300ft. Dots in the third figure are measured data, curve is predicted using model.

Figure 2-9: General Pressure - temperature Relationships in Petroleum Reservoirs (shaded), along typical geothermal gradients in sedimentary basins and P-T Conditions in experimental studies (Manning 2003)
Figure 2-10: Illite% in I/S vs. Time (Huang, 1993). The KCl concentration is 1 mol/L. Reaction rate increases with temperature.

Figure 2-11: Illite% in I/S vs. Time (Huang, 1993). The temperature is 275 C. Reaction rate increases with KCl concentration.
Chapter 3

Smectite and Illite

The objective of my research is to study the smectite-to-illite transformation. There are two major challenges in my research: 1. to transform smectite to illite in a laboratory within a practical time scale 2. to analyze the transformed clay sample and quantify the smectite, illite and other minerals in the sample.

Overcoming these challenges need the fundamental knowledge of clay minerals. Thus, this chapter is dedicated to provide the general structural features of clay minerals from the assembly of tetrahedral sheet and octahedral sheet to layer stacking order of smectite and illite. The most common way to study a clay mineral is to study its x-ray diffraction (XRD) pattern. The understanding of clay mineral microstructure is essential to understand the x-ray diffraction pattern which is presented in Chapter 4 and Chapter 5.

3.1 Clay Minerals

Clay is generally a fine-grained natural rock or soil material. But different professions have different definitions of clay. To a geotechnical engineer, clay is a kind of fine-grained soil particle. They are interested in the plasticity, compressibility and shear strength of a clay rich soil. To a geologist, clay is classified as phyllosilicates, or layered silicates, most of which are crystalline. The classification of clay minerals is based on their unique crystal structure. The particle size of clay minerals is less than
2μm. Clay minerals are formed by a special process. They are grown as crystals from the ground up (Moore and Reynolds, 1997). Their size is limited by the very slow kinetics that prevail in the low-temperature environments in which they form, and by the high density of crystal defects that would destabilize them as larger crystals.

3.1.1 General Structural Features

In the field of clay mineral, there are numerous terminologies and jargons. It is nice to review them before we jump into the clay mineral discussion.

Unit Cell of a Crystal

A crystal is a highly ordered structure in which the atoms are engaged in a infinitely repeating organization in all 3D dimension. A unit cell is the smallest unit of volume that contains all of the structural and symmetry information to build up the macroscopic structure.

We can think unit cell as a box. It contains one or more atoms inside the box. The lengths of box edges are described by a, b and c. The angles between the box edges are describe by α, β and γ. Unit cell is classified according to its edge lengths and angles. There are 7 types of unit cell as shown in Fig. 3-1. Fig. 3-8 shows the unit cell of montmorillonite, which is a species of smectite. In section 3.3, we will discuss the unit cell for smectite and illite in detail.

Miller Index

The Miller index is a notation system in crystallography for planes in crystal lattices. The notation (hkl) denotes the orientation of a plane. The notation [hkl] denotes the direction of a vector. For clay minerals, the unit cell usually extend in (001) plane as shown in Fig.3-2 and form platy morphology. In addition to orientation of (001) plane, Fig. 3-2 also displays the orientations for other hkl planes.
Tetrahedral Sheet

The Tetrahedral and octahedral sheets are the basic building blocks of phyllosilicates or clay minerals. Fig. 3-3 shows the formation of a tetrahedral sheet. The tetrahedron consists of one silicon atom in the center and four oxygen atoms. The tetrahedron repeats itself to form a plane known as tetrahedral sheet. The tetrahedral sheet is often represented by a trapezoid.

Octahedral Sheet

Fig. 3-4 shows the formation of a octahedral sheet. The octahedron unit has one aluminium or magnesium in the center and six hydroxyl ions. The octahedron repeats itself to form a plane known as an octahedral sheet. The octahedral sheet is represented by a rectangle. (Mitchell et al., 1976).

Clay Layer and Interlayer

Tetrahedral sheet(T) and octahedral sheet(O) stack in the direction that is perpendicular to the (001) plane in ionic and covalent bonding to form layers. There are two types of stacking mode: 1) 1:1 basic unit 2) 2:1 basic unit as illustrated in Fig.3-5.

The 1:1 basic unit layer has 1 tetrahedral sheet and 1 octahedral sheet. The typical examples are kaolinite and halloysite mineral. The 2:1 basic unit layer has 2 tetrahedral sheet and 1 octahedral sheet to form a sandwich structure. Illite, smectite and vermiculite are the examples for 2:1 basic unit layer. Fig. 3-5 illustrates the clay layer synthesis pattern for different clay minerals.

In particular, Fig. 3-8 displays the unit cell for montmorillonite which is a species of smectite, the clay layer and interlayer are labelled in the figure. Montmorillonite has two tetrahedral sheets and one octahedral sheet.

Interlayer is the space between two clay layer. In section 3.4, we will discuss properties about the interlayer in detail.
Basal Spacing or d-spacing

The distance between two clay layer is called basal spacing or d-spacing. Basal spacing is also the length of unit cell along [001] direction. Fig.3-8 labels the basal spacing for montmorillonite unit cell.

3.2 Smectite and Illite

The illite group minerals are characterized by a d-spacing of about 10 Å which remains fixed in dry and wet condition. The unit cell of illite group is monoclinic. The lengths of unit cell dimension are different. The values for a, b and c are around 5.2 Å, 9.0Å and 10.0Å respectively. Angles $\alpha$ and $\gamma$ are equals to 90°. Angle $\beta$ is not equal to 90°, the value varies depending on the illite polytype. Illite polytype is caused by layer stacking disorder which will be explained in Section 3.3. The interlayer potassium cations tightly bond illite clay layers together. There is little or no water layer inside the interlayer space. Fig. 3-9 shows a 3D model for illite. The purple is the tetrahedral sheet, the cyan is the octahedral sheet. Between two illite clay layers, the purple dots are potassium cations. (Deer et al., 2011)

The smectite group minerals do not have a fixed value for d-spacing[001]. The d-spacing varies from 10Å to 15Å commonly depending on its hydration state and types of interlayer cations. Smectite can take in water as zero, single, double or triple layers of water as shown in Fig.3-10. The d-spacing does not change linearly with hydration state but discretely. Single, double, triple layers correspond to a d-spacing of around 12.5Å, 15.4Å, and 18.5Å respectively for sodium saturated smectite. If there is no water layer in the interlayer space, the d-spacing of smectite drops to 10 Å. However, d-spacing recorded by XRD can be continuous between 10 Å to 18.5 Å because the XRD records a bulk sample which contains thousands of smectite layers with different hydration states. The unit cell of smectite group is also monoclinic, with a, b and c being around 5.2 Å, 9.0 to 9.2Å and 10 to 15Å respectively. Fig. 3-8 shows the unit cell for montmorillonite. The red dots are oxygen atoms, the milky dots are silicon atoms, the grey dots are aluminum atoms. They are bonded by
Smectites have many subgroups and variations, because smectites have loose interlayer bonding and more atomic substitution in the clay layer. Smectites are classified according to their structural formula. Fig. 3-6 lists the names and their structural formulas. The first row and third row in Fig. 3-6 are the elements in the tetrahedral sheet. The second line is the elements in the octahedral sheet. For instance, montmorillonite has just Si in the tetrahedral sheets and Al, Mg and Fe in the octahedral sheet. In reality, the smectites are found in the sedimentary rock are more complicated. We need to analyze the elemental composition to calculate their structural formula.

### 3.2.1 Interlayer Cations of Smectite and illite

The clay layer surface is negatively charged due to isomorphous substitution in the clay layer. Illite clay layer is usually more negatively charged than smectite clay layer as shown in Fig. 3-7. In order to achieve charge balance, cations are attracted to the clay layer surface.

There are two types of cations: exchangeable and non-exchangeable. The exchangeable cations are able to move in and out of the interlayer while the non-exchangeable ones are fixed between two clay layers. The interlayer cations for smectite are exchangeable, but the interlayer cations for illite are fixed between the illite layers.

In the sea water, the most abundant cation is Na\. Clay minerals in the sedimentary basin are found mostly sodium saturated. Cations with higher valence have higher affinity to the clay layer, because the local charge density for higher valence cation is greater. So $Mg^{2+}$ and $Ca^{2+}$ are attached to clay layers tighter than $Na^+$. According to Eberl (1980), affinity of different cations to montmorillonite clay surface follows:

$$Al^{3+} > Ca^{2+} > K^+ > Na^+$$

(3.1)
The most common interlayer cation for smectite is \( Na^+ \), sometimes \( Mg^{2+} \), \( Ca^{2+} \) or \( K^+ \). Depending on smectite hydration state, there are water layers between clay layers. The interlayer cations for illite is predominantly \( K^+ \), but there is no water layer between clay layers as shown in Fig.3-7.

### 3.3 Layer Stacking Disorder

Fig. 3-11 shows an example of layer stacking disorder. This high resolution transmission electron microscopy (HRTEM) image is recorded along [100] axis by Kogure Lab at University of Tokyo. It displaces a stacking fault of illite by layer rotation near the bottom of the image. In addition to layer rotation, researchers also found translational stacking disorder in the clay minerals. Fig. 3-12 illustrates translation and rotation of one layer with respect the one under it along z-axis. Each hexagonal card in Fig. 3-12 represents one clay layer.

For illite, we observe rational stacking disorder. The illite layer translates a distance of \( a/3 \) to form 1M polytype, where \( a \) is the length of illite unit cell along x axis. In addition, illite layers can rotate plus and minus 60° to form 2M\(_1\) polytype, or rotate 120° successively to form 3T polytype.

On the other hand, smectite forms turbostratic stacking disorder. This type of disorder is present in almost all smectite minerals. The layers are displaced from each other in the x-y plane by random amounts and are rotated about the z-axis by random amounts. Fig. 3-8 shows such an arrangement.

The random stacking disorder of smectite is due to the fact that smectite interlayer bonding is weak. Illite has stronger interlayer bonding compared with smectite. The surface structure of illite layers is keyed on the interlayer \( K^+ \), thus, the stacking disorder is rational.
3.4 Mixed Layer Mineral

The mixed-layered mineral (MLM) is formed of two or more kinds of intergrown minerals stacking along z axis. Interstratifications of more than two components are quite rare. The most common and well studied case is illite/smectite (I/S), and I/S is also the focus of my research, but MLM also includes chlorite/smectite, illite/chlorite, and etc..

MLM is not a physical mixture of the components but rather a statistical crystal (Nadeau et al. 1984). The McEwan structure model provides a one-dimensional description of smectite and illite mixed layer along the [001] direction or z-axis. Layers of illite and smectite are pictured as intimately interstratified in the Fig. 3-14. McEwan structure is also a super cell that contains N unit cells, where N is number of clay layers. In order to describe how smectite and illite are mixed-layered, we need to introduce Reichweite concept. Reichweite provides a way to represent the ordering and sequence of the MLM. I/S has a N value around 10.

3.5 Ordering of I/S by the Reichweite Concept

As mentioned in Chapter 2, the percentage of illite increases with depth in the I/S phase as a result of smectite-to-illite transformation. The stacking sequence of I/S is affected by the percentage of each phase. We can describe stacking sequence statistically with ordering using the Reichweite concept.

Reichweite is a German word, which translates as “the reach back”. The Reichweite concept describes the probability of the occurrence of a layer. To be more specifically, Reichweite is the probability, given layer A, of finding the next layer to be B. If you consider a ISII(R3) stack, a Reichweite value of 3 means: the first illite layer has influence reaches three positions to the last illite layer, or each smectite layer is surrounded by at least three illite layers (Altaner & Bethke, 1988). Only values R0 to R3 are reported in the literature for I/S MLM (Ufer et al., 2012).
3.5.1 Statistical treatment of I/S ordering

Drits and Tchoubar (2012) provided mathematical description of MLM order. The junction probability \( P \) and proportions \( W \) of layer stacks is necessary for a quantitative description of MLM. If we consider a stack of \( N \) layers which consists of smectite(S) and illite(I). Then we have

\[
W_S = \frac{N_S}{N} \quad (3.2)
\]
\[
W_I = \frac{N_I}{N} \quad (3.3)
\]
\[
W_S + W_I = 1 \quad (3.4)
\]

where \( W_S \) and \( W_I \) are the relative proportions in the minerals, \( N_S \) and \( N_I \) are the number of smectite and illite layer in the stack.

If we consider SS, SI, IS and II pair, we will have

\[
W_{ij} = \frac{N_{ij}}{N} \quad \text{for } i, j = S, I \quad (3.5)
\]
\[
\sum_i \sum_j W_{ij} = 1 \quad (3.6)
\]

Expressions defining the relative abundances can be written using probabilities \( P \).

\[
W_{ij} = W_i P_{ij} \quad \text{for } i, j = S, I \quad (3.7)
\]
\[
P_{ii} + P_{ij} = 1 \quad (3.8)
\]

For random order(R0), \( P_{II} \) the probability that an illitic layer follows another one is equal to the probability that I follows S and simply depends on the proportion of I.

\[
P_{II} = P_{SI} = W_I \quad (3.9)
\]
and we can compute:

\[ P_{IS} = 1 - P_{II} \]  \hspace{1cm} (3.10)
\[ P_{SS} = 1 - P_{SI} \]  \hspace{1cm} (3.11)

For R1 order, the equation 3.9 no longer holds, the probability that an illitic layer follows another one depends on the nature of the preceding layer and the proportion of I. For instance, if an illitic layer follows a smectitic layer, the probability of \( P_{SI} \) is:

\[ W_I = W_{II} P_{II} + W_{SI} P_{SI} \]  \hspace{1cm} (3.12)
\[ P_{SI} = (W_I - W_{II} P_{II})/W_S \]  \hspace{1cm} (3.13)

From Equations 3.8, 3.10 and 3.11, we can figure out \( P_{SS} \) and \( P_{IS} \).

For R2 and R3 order, the computation becomes too sophisticated to carry out manually. Fig. 3-15 shows the smectite and illite sequence with different ordering and different percentage of illite. Each line represents a MacEwan crystalline with z-axis projected horizontally. Each I/S super cell has 15 clay layers (\( N=15 \)). The dot stands for smectite, and I for illite. For RO random ordered I/S, the possible sequences are computed based on the method discussed in this section and are presented in the figure a b and c. As the order increases, average \( W_I \) is significantly higher than random ordered MLM. Illite layers also become more clustered with increasing ordering.

In summary, statistical treatment of I/S ordering is an efficient way to describe the MLM. It greatly reduces the computational effort if we have to use the explicit method.
Edges and angles

Monoclinic
\( a \neq b \neq c \)
\( \alpha = \gamma = 90^\circ \neq \beta \)

Cubic
\( a = b = c \)
\( \alpha = \beta = \gamma = 90^\circ \)

Tetragonal
\( a = b \neq c \)
\( \alpha = \beta = \gamma = 90^\circ \)

Orthorhombic
\( a \neq b \neq c \)
\( \alpha = \beta = \gamma = 90^\circ \)

Hexagonal
\( a = b = c \)
\( \alpha = \beta = 90^\circ, \gamma = 120^\circ \)

Rhombohedral
\( a = b = c \)
\( \alpha = \beta = \gamma = 90^\circ \)

Triclinic
\( a \neq b \neq c \)
\( \alpha \neq \beta \neq \gamma \neq 90^\circ \)

---

Figure 3-1: Unit Cell for a Crystal (Averill and Eldredge, 2006)

---

Figure 3-2: Plane Orientations Denoted by Miller Index (Averill and Eldredge, 2006)
Figure 3-3: Formation of Tetrahedral Sheet (after Mitchell et al., 1976)
Figure 3-4: Formation of Octahedral Sheet (after Mitchell et al., 1976)
Oxygen or Hydroxyl

Packed according to charge and geometry

Repeated to form a sheet

Tetrahedral

Octahedral

Stacked in ionic and covalent bonding to form layers

1:1 semi-basic unit

2:1 semi-basic unit

Stacked in various ways

Stacked in various ways

Figure 3-5: Synthesis Pattern for the Clay Minerals (Mitchell et al., 1976)

Figure 3-6: Structural Formula for Smectites (2015 DTTG Workshop). The first row and third row are elements for tetrahedral sheet. The second row contains the elements for octahedral sheet. Minerals in smectite group are further classified according to their structural formula.
Smectite and Illite

Smectite

Illite

Figure 3-7: Structure for Smectite and Illite (Mitchell et al., 1976). The d-spacing for smectite varies from 10 to 15 Å. The d-spacing for illite is 10 Å. The potassium smectite contains water layers in the interlayer whereas illite has no water layer.

Figure 3-8: Unit Cell for Montmorillonite (AMCSD Database). The red dots are oxygen atoms, the milky dots are silicon atoms, the grey dots are aluminum atoms. They are bonded by covalent bond. This unit cell contains two water layer. The d-spacing is 15 Å.
Figure 3-9: 3D Model of Illite Structure (Deer et al., 2011). The purple tetrahedral plane is the tetrahedral sheet, the cyan octahedral sheet is the octahedral sheet. Between two illite clay layers, the purple dots are potassium cations.

Figure 3-10: Interlayer Water inside smectite (Moore and Reynolds, 1997) Smectite can take in water as zero, single, double or triple layers of water. Single, double, triple layers correspond to a d-spacing of around 12.5Å, 15.4Å, and 18.5Å respectively for sodium saturated smectite.
Figure 3-11: TEM Image of Stacking Disorder in illite (Kogure Lab at U of Tokyo). At the lower part of image, we can see the stacking disorder.

Figure 3-12: Stacking Disorder (Moore and Reynolds, 1997). Each hexagonal card represents one clay layer.
Figure 3-13: Turbostratic stacking of smectite. (Moore and Reynolds, 1997). The translation and rotation between clay layers are random.

Figure 3-14: McEwan Structure and Reichweite Ordering (Altaner and Bethke, 1988). McEwan crystalline is also a super cell that contains N layers of unit cell. S stands for smectite, i stands for illite.
Figure 3-15: McEwan Structure and Reichweite Ordering (Altaner and Bethke, 1988)
Each line represents a MacEwan crystalline with z-axis projected horizontally. Each I/S super cell has 15 clay layers. The dot stands for smectite, and I for illite. The sequences of I/S are computed using statistical method by Drits and Tchoubar (2012) depending on the illite percentage and ordering of I/S.
Chapter 4

Quantification of Clay Minerals

The previous chapters present a brief description of the clay mineral structure; this chapter discusses the methods used to determine the composition of the clay minerals by x-ray diffraction (XRD).

The quantification of a soil sample consists of two parts: 1) random powder diffraction for non-clay fraction 2) textured or oriented diffraction on (00l) peaks for clay fraction (< 2μm). Both methods are very important for quantification of the mineral transformation, but my thesis focuses on the clay fraction. So this chapter only covers the textured diffraction method.

Before a soil or rock sample is ready for XRD, the sample has to be chemically treated to remove impurities such as organic matter, iron oxides and carbonates. Then sample needs to be Ca²⁺ cation saturated for a positive identification of smectite peak. I did several XRD scans on GoM-EI sample without impurity removal and cation saturation for a quick qualitative analysis. Samples sent to Shell for quantitative analysis had been chemical treated and cation saturated.

After impurity removal and clay fraction separation, sample is ready for the preparation of oriented clay slide. There are different ways to prepare a oriented sample. This chapter discusses glass method and filter transfer method in detail, compares the advantages and disadvantages between these two methods. The XRD scans that I ran were prepared using glass method. The XRD pattern scanned by Shell were prepared using filter transfer method. In general, glass method requires less equipment and the
technique is easy to master, but the quality of XRD obtained from glass method is not good for quantitative analysis. The filter transfer method provides good quality XRD pattern for quantitative analysis but this method requires special equipment and the technique used requires extensive training.

4.1 How does XRD work?

The first diffraction experiment was conducted by Von Laue in 1912, after a century of development, accurate phase quantification of clay mineral is still a challenge. Reynolds once stated, “the amount of effort for preparing a good sample is enormous. The effort is here to remove uncertainty Analysis of clays by XRD methods should probably be considered excellent if the results are accurate to about 10% of the amounts present, and, perhaps, 20% if the concentrations are less than 10%.”

The atoms arrayed in a crystalline structure cause a beam of incident x-rays to diffract into many specific directions. The x-ray diffraction method records the angles and intensities of the diffracted beams. One can distinguish the type of minerals and the composition of different mineral types by analyzing the diffraction pattern.

Fig. 4-1 explains how x-ray diffraction work. In general, the incident x-ray is scattered by the sample to all directions. If the sample is a crystalline material, for parallel planes of atoms, with a spacing $d_{hkl}$ between the planes, constructive interference only occurs when Braggs law (equation 4.1) is satisfied. These parallel planes produces a diffraction peak only at a specific angle $2\theta$.

$$n\lambda = 2d_{hkl} \sin \theta \quad (4.1)$$

Where $\lambda$ is the wavelength of x-ray and $d_{hkl}$ is the basal spacing between two lattice planes, $\theta$ is the incident angle.
4.2 Textured Sample Diffraction

In chapter 3, we cover the general features about clay minerals. Most of clay minerals have platy morphology and perfect (001) cleavage. Thus, we can use textured or oriented sample diffraction to prepare a clay film enhancing 001 reflection. The textured sample diffraction provides the most diagnostic pattern for the simple and the mixed-layered clay minerals, because it greatly enhanced the diagnostic 00$l$ diffraction. Whereas in three-dimensional studies or random powder diffraction, all the peaks are weak, only a small portion of crystallites have the required orientation for a particular $hkl$ direction. The weak intensity of the peaks makes it hard to interpret the XRD pattern.

4.3 How to Prepare a Textured Sample

4.3.1 Chemical Treatment

We need to remove impurity from a soil or rock sample before it is ready for XRD. The procedure involves removal of iron oxides, organic materials and carbonates. Treatments are not limited to these three depending on the material you have. Jackson (2005) provides a detailed description of how to remove impurities.

4.3.2 Saturating the Clay Minerals with Different Cations

Fig. 4-2 shows that the d-spacing of a smectite depends on what cation it has. $Na^+$ saturated montmorillonite has the smallest d-spacing and weakest intensity. On the other hand, $Ca^{2+}$ or $Mg^{2+}$ saturated montmorillonite has greater d-spacing and peak intensity.

In order to have a positive identification of smectite, the sample is saturated with $Ca^{2+}$ or $Mg^{2+}$. The technique is quite simple. We can submerge the sample with 0.1 M of $CaCl_2$ or $MgCl_2$. An exchange reaction will occur. Cation A usually $Na^+$ or $K^+$ will be replaced by the target cation. The clay mineral will become saturated with the target cation after replacing the liquid with fresh solution for 3 to 5 times.
After saturating, we need to wash away the excess $Ca^{2+}$ or $Mg^{2+}$ with deionized water. To test if the excess salt is washed, we can add a drop or two of $AgNO_3$ into the solution. If no $AgCl$ precipitation is observed, then the washing is done, otherwise, repeat washing.

### 4.3.3 Particle-size Separation

Clay particle tends to stick to the surface of bigger particle or attach to each other. To have a accurate analysis, we need to deflocculate the soil suspension before we separate. Sodium hexametaphosphate is used to disperse soil suspension. A concentration of $10^{-3}$ to $10^{-4}$ mol/L is enough to deflocculate. With the sample well dispersed, we can start to separate the particle. Stoke’s law calculates the settling velocity $V$ of a particle with a density of $\rho_s$ fall through a fluid with a density of $\rho_w$ and a viscosity of $\eta$.

$$V = \frac{g(\rho_s - \rho_w)D^2}{18\eta} \quad (4.2)$$

We can calculate the time required for desired particle size separation at certain settling distance.

$$t = \frac{h}{V} \quad (4.3)$$

Where $t$ is the time, $h$ is the height and $V$ is the velocity of a particle. For a settling distance of 5cm and a mineral density of 2.65, the settling time for 2$\mu$m diameter particle is 3 hours and 50 minutes. We can fill a test tube with soil suspension, wait for required time, then extract the fluid above the settling distance using a syringe (Fig. 4-3).

### 4.3.4 Prepare the Textured Slide

After we separate the clay fraction from the sample, we can make clay slide for XRD. There are several methods we can use depending on the application. They are: 1. glass slide 2. smear method 3. filter transfer 4. porous plate. We will discuss glass slide and filter transfer method in the later section because they are relatively easy
to prepare and produce good enough x-ray pattern for quantification analysis. The smear method is for qualitative analysis only. The porous plate method requires a lot of training to have a good quality sample. I had prepared samples using glass method for qualitative analysis. Samples scanned by Shell were prepared by filter transfer method.

**Glass Method**

This method is easy to use; requires minimum amount of equipment. We can simply use a pipette to drop clay suspension on a glass substrate or zero background holder (Fig. 4-4). Although this method is easy to use, but the clay film is usually too thin for accurate diffraction intensities at high diffraction angles. Another issue associated is: the film is usually particle size segregated with finest material on the top. Most importantly, the orientation is only fair. The platy particle is not perfectly oriented horizontally. Because of these issues, the glass method is not recommended if you have access to vacuum filter apparatus.

**Filter Transfer Method**

This method requires a vacuum filter apparatus. The suction forces platy clay minerals to lie flat on the substrate. Clay minerals using this method are well oriented compared to the ones using glass method. Clay suspension is added to the top container. Suction will draw down the water; meanwhile a filter separates the clay mineral from water and forms a homogeneous layer of clay mineral (Fig. 4-5). The suction time can be as long as necessary to get a layer that is thick enough, so that at high diffraction angle, the x-ray beam can not penetrate the clay film. After we have a thick enough clay film, we can transfer the wet clay film onto a glass substrate as shown in Fig. 4-6. Filter and clay film are center-positioned near the glass slide and then quickly and smoothly lightly rolled across the slide to transfer the clay film to the slide. Any hesitation or jerky motion during the transfer may cause rippling of the film and disrupt the preferred orientation.

In summary, glass method is good for qualitative analysis, the orientation of clay
<table>
<thead>
<tr>
<th></th>
<th>Glass Method</th>
<th>Filter Transfer Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Application</td>
<td>qualitative analysis</td>
<td>quantitative analysis</td>
</tr>
<tr>
<td>Textured Orientation</td>
<td>fair</td>
<td>perfectly horizontal</td>
</tr>
<tr>
<td>Equipment</td>
<td>easy to access</td>
<td>requires specially designed vacuum apparatus and ultra-fine filter</td>
</tr>
<tr>
<td>Technique</td>
<td>easy to master</td>
<td>needs training</td>
</tr>
<tr>
<td>Thickness of clay film</td>
<td>thin</td>
<td>thick</td>
</tr>
</tbody>
</table>

Table 4.1: Comparison between glass method and filter transfer method

particle is not perfectly horizontal, the thickness of clay film is rather thin. The glass method is easy to use, the equipments are easy to access, no special training is required.

While filter transfer method is used for quantitative analysis, the clay particle is perfectly orientated, the thickness of clay film is thick. But filter transfer method requires specially designed vacuum apparatus and ultra-fine filter. It also requires training to use the equipment.

Air Dried Sample

For the samples prepared using glass method, we can simply let them dry at room temperature for 24 hours. We can also put the clay film into the oven. Drying usually takes about 1 hour at 90°C. For the filter transfer method, the film will dry out much faster. The samples I prepared were air-dried at room temperature for 24 hours.

Ethylene Glycol Solvated Sample

Fig. 4-7 shows how d-spacing of montmorillonite increases with relative humidity. In the air dried condition, the smectite peak is affected by the humidify. We usually treat the sample with ethylene glycol to minimize the uncertainty. The advantages of using ethylene glycol as compared with water are: 1) increased intensities of second and higher order reflections and 2) development of relatively stable, two-layer EG molecules. Fig. 4-8 is an example of how ethylene glycol salvation affects pretest GoM-EI XRD pattern. The smectite peak is expanded from 15 Å in air dried condition to 17 Å in ethylene glycol solvated condition. In addition, the mixed layered I/S peaks
show up at higher angles.

The best way to solvate a sample is to expose the sample to the vapor of ethylene glycol for at least 8 hours at 60 C. We can put the prepared clay slide in a desiccator, add 100ml of ethylene glycol to the desiccator, and put the setup in a oven. To avoid evaporation of ethylene glycol from sample during transpiration and waiting time, we can carry the desiccator to the x-ray machine room. It is best to finish the whole process within an hour, for longer times, the glycol will evaporate away sufficiently to affect the expansion of clay minerals.

4.4 XRD Modeling and Quantification

This section provides a general idea of how to quantify clay minerals using modeling approach.

The position of the peaks in a XRD pattern gives the identification of the clay minerals. The intensity of the peaks indicates the relative abundance of the phases. To figure out the exact percentage of each phase in a mixture, we need to calculate XRD profile using a theoretical structure model. This method is often referred as Rietveld refinement method. Rietveld method was developed as a substitute for structure refinement from single crystal data.

Rietveld method is an optimization algorithm that minimizes the weighted sum of square of the difference between the experimental XRD pattern and the calculated XRD profile (equation 4.4)

\[
\sum_i w_i [y_i (exp.) - y_i (cal.)]^2 \rightarrow min
\]

(4.4)

\[
w_i = \frac{1}{y_i}
\]

(4.5)

Where \(w_i\) is the weighting factor, \(y_i (exp.)\) is the experimental XRD pattern, \(y_i (cal.)\) is the calculated XRD profile. The experimental XRD pattern is obtained from sample.

Fig.4-9 explains the method for calculating mineral composition. First step is to
find the structure model for each phase in the sample. The structure model contains information about the atomic positions and lattice parameters of the unit cell. Structure factor $F_{hkl}$ is the matrix form of structure model. Second step is to calculate the intensity using the structure models obtained in step one. The calculated XRD profile intensity is a function of Lorentz factor $L$, polarization factor $P$, absorption correction $A$ and structure factor $F$ as shown in equation 4.6. $P$ and $L$ are angle dependent functions, they stay the same for the same incident angle $\theta$. $A$ corrects the loss of intensity inside a particle, but it is negligible in perfectly oriented sample.

$$I_{hkl} \propto APL|F_{hkl}|^2 \quad (4.6)$$

Third step is to fit the calculated intensity to measured XRD pattern by optimizing parameters such as scale factor, abundance of each phase, the preferred orientation correction factor, and etc.. The four step is to check the goodness of fit. We can simply compare the shape of calculated XRD profile with the measured XRD profile to estimate the goodness of fit. Mathematically, weighted goodness of fit is determined by $R_{wlp}$ in equation 4.7.

$$R_{wlp} = \sqrt{\frac{\sum w_i [y_i (exp.) - y_i (cal.)]^2}{\sum w_i y_i^2 (exp.)}} \quad (4.7)$$

If $R_{wlp}$ is lower than 10%, the algorithm will output the result for mineral composition. If the goodness of fit is bad, the algorithm will go back to step one, change and optimize the structure model. Using a iterative approach, we can refine the initial not ideal structure model to the one which is closer to the true structure.

As mentioned in chapter 3, clay minerals are not perfect crystalline material, and the layer stacking disorder in illite and smectite is ubiquitous. If there are mixed-layered mineral in sample, the single unit cell structure model approach will not converge to a solution. For mixed-layered mineral(MLM), the structure model is built up using $N$ layers of unit cell. In addition, it needs to consider the ordering of the MLM using Reichweite concept discussed in section 3.5
Figure 4-1: X-ray Diffraction Geometry. The incident x-ray is scattered by the lattice plane. When the scattered x-ray satisfies Bragg’s law, it generates a coherent diffraction peak. $\theta$ is the scattering angle.

Figure 4-2: D-spacing of Montmorillonite for Different Interlayer Cations, (Ghosh & Tomar, 1974) The smectite d-spacing [001] changes with different interlayer cations.
Figure 4-3: Particle Separation by Timed Sedimentation Method

Figure 4-4: Glass Method: Clay Suspension on Zero Background Holder
Figure 4-5: Filter Transfer Method (modified after USGS)

Figure 4-6: Filter Transfer Method (photo courtesy of USGS). Transferring the clay film from a filter to a glass substrate.
Figure 4-7: D-spacing of Montmorillonite under Different R.H. (Ghosh & Tomar, 1974). The smectite d-spacing [001] changes with hydration state.

Figure 4-8: Glycolated and Ca$^{2+}$-saturated Pretest GoM-EI vs Air Dried
Structure Model

Intensity calculation based on structure model
\[ I_{\text{int}} \propto A P F I_{\text{int}}^2 \]

Fitting the calculated intensity to measured XRD pattern

Check goodness of fit

Output result: Phase Abundance

Good fit

Bad fit

Variation and optimization of structure model

Figure 4-9: XRD Quantification Algorithm
Chapter 5

Equipment and Procedures

This chapter covers the equipment and procedures used in hydrothermal reaction of GoM-EI material. The first generation reactor can tolerate temperature up to 200° C, and the second generation reactor can tolerate temperature up to 350° C. The first generation reactor was designed by the MIT Geotechnical Engineering Laboratory, while the second generation reactor was purchased from Col-Int Tech, but modified to accommodate specific requirements of this project.

5.1 Pressure and Temperature Condition for the Reaction

In geological setting, the transformation takes up to millions of years. In order to cause the transformation in a human time scale or more time effective period, hydrothermal reactions were conducted in elevated temperature, much higher than that in the basin for burial diagenesis.

There were seven hydrothermal tests conducted: IS 01 - IS08. IS05 test failed due to chemical corrosion of tubes during cooking. The temperature and pressure conditions are listed in Table 5.1. Temperature ranges from 150° C to 300° C. Pressure varies from 1.5 MPa to 9.0 MPa. Standard run time is 18 days and extend run time is 29 days. The critical pressure is the pressure on the saturated vapor curve for a given
temperature. The pressure for each test has to be greater than the critical pressure at that reaction temperature in order for the reaction to occur in one liquid phase. The red dots in the phase diagram (Fig. 5-1) illustrate that all test conditions are inside liquid phase.

![Phase Diagram for Pure Water](image)

**Figure 5-1: Phase Diagram for Pure Water**

The Antoine equation (4.1) was used for calculating saturated vapor pressure at a given temperature for water.

\[
P = 10^{A - \frac{B}{T+C}}
\]  

(5.1)

Where \( P \) is saturated vapor pressure in mmHg, \( T \) is the temperature in °C, \( A, B \)

<table>
<thead>
<tr>
<th>Test #</th>
<th>Temperature (°C)</th>
<th>Time (days)</th>
<th>Pressure (MPa)</th>
<th>Critical Pressure (MPa)</th>
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<tbody>
<tr>
<td>IS01</td>
<td>200</td>
<td>18</td>
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</tr>
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<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 5.1: Temperature and Pressure Setting for Tests

The Antoine equation (4.1) was used for calculating saturated vapor pressure at a given temperature for water.
and C are constants. Note that the Antoine equation has different coefficients to fit a temperature range from 1°C to 100°C and 100°C to 374°C. The values for A, B and C are listed in Table 4.2.

<table>
<thead>
<tr>
<th>water temperature range</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1°C to 100°C</td>
<td>8.07131</td>
<td>1730.63</td>
<td>233.426</td>
</tr>
<tr>
<td>100°C to 374°C</td>
<td>8.14019</td>
<td>1810.94</td>
<td>244.485</td>
</tr>
</tbody>
</table>

Table 5.2: Parameters for Antoine Equation

The pressure obtained from the Antoine equation is in mmHg, not in Pascal. It is easy to convert from mmHg to Pascal using equation 5.2:

\[ 760\text{mmHg} = 101.325\text{kPa} = 1.000\text{atm} \]  

(5.2)

## 5.2 The Critical Pressure of KCl solution

The previous section discusses the phase relation of pure water, but many of the physical properties of a solution differ significantly from pure water. In general, the critical pressure of a solution is lower than that of water. A schematic (Fig. 5-2) explains this phenomenon qualitatively. For example, in glucose solution a portion of the surface area is occupied by nonvolatile glucose molecules rather than by volatile water molecules. As a result, fewer water molecules can enter the vapor phase per unit time. Consequently, the vapor pressure of the solution decreases compared with the vapor pressure of the pure water.

In my test, 3mol/L KCl solution was used for the pore fluid. The critical pressure of KCl solution was calculated by Raoult’s Law (equ. 4.3).

\[ P_A = X_A P_A^\circ \]  

(5.3)

\[ X_A = \frac{n_{H_2O}}{n_{K^+} + n_{Cl^-} + n_{H_2O}} = \frac{50.46\text{mol}}{56.46\text{mol}} = 89.37\% \]  

(5.4)

Where \( P_A^\circ \) is the critical pressure for pure water; \( P_A \) is the critical pressure for solution; \( X_A \) is the mole fraction of water. Water molecules take up 89% of the sum...
Figure 5-2: A model depicting why the vapor pressure of a solution is less than the vapor pressure of pure water. The vapor pressure of c) is less than that of a).

of the water molecule, $K^+$ and $Cl^-$ (equ. 4.4) in a 3mol/L KCl solution. Therefore, there is a 11% reduction of critical pressure.

## 5.3 Equipment for Hydrothermal Reaction

There were two sets of reactors used in my research. IS01 test was conducted using the first generation reactor. The rest of tests were conducted using the second generation reactor. These two sets of reactors are similar in that they provide heat and fluid cell pressure to the sample.

### 5.3.1 First Generation Reactor

The first generation reactor is made of stainless steel and is sealed with rubber o-rings. The reactor consists of three pieces: cylindrical cell wall, top and bottom cap. The reactor can hold up to 3 g dry mass of material in a ceramic cup(Fig. 5-4). A Viton o-ring was used to seal the reactor. During the test, the reactor was inside an oven that provided heat to cook the sample.

The temperature rating for this reactor is $200^\circ C$. The maximum temperature is limited by the temperature rating of o-ring. In order to cook the sample at a higher temperature, I launched an investigation of different types of sealing material. Details of sealing material are discussed in the 5.3.3.
Figure 5-3: First Generation Reactor. Pressure-volume actuator (PVA) provides external cell pressure. During the test, reactor is inside the oven.

Figure 5-4: GoM-El Pretest Sample inside a Ceramic Cup
5.3.2 Second Generation Reactor

The need for a second generation reactor emerges when the reaction needs to perform at a higher temperature. The second generation reactor was purchased from Col-Int Tech and modified to accommodate custom requirements. Fig. 5-5 shows the equipment used for my tests. The reactor is made of Cr-Ni-Ti stainless steel 316 to accommodate the high temperature and chemical corrosive environment. This reactor can tolerate temperature up to 400°C and pressure up to 30 MPa. The cell pressure is injected externally by pressure-volume actuator (PVA). The ceramic heating element attached to the bottom of the reactor provides energy to heat the sample. The thermocouple measures the temperature inside the chamber.
5.3.3 Sealing Material

The combination of high pressure, elevated temperature and corrosive chemical environment make it becomes difficult to find the right material for sealing. Rubber o-rings are the traditional sealing material used for triaxial tests and CRS tests. Rubber o-rings can seal well under room temperature and they provide good chemical resistance to KCl solution. The most common types of rubber o-ring are Viton and Kalrez. The temperature rating for the rubber o-ring is from roughly $-20^\circ C$ to $200^\circ C$. When exposed to a temperature that is higher than the rating, the rubber o-ring will fail to function due to thermal degradation and decompression.

In addition, I also investigated metallic seal and graphite gasket. Metallic seal can seal up to $700^\circ C$. It is easy to install and maintain but the price for an individual order is high.

Rather than looking for new sealing material, I found a commercial off-the-self hydrothermal reactor. The second generation reactor uses a graphite gasket to seal. The temperature rating for this type of graphite gasket is $350^\circ C$. The pressure rating for graphite gasket is 2000 psi; for a reinforced graphite gasket, the rating can go up to 5000 psi.

Although, this graphite gasket satisfies the requirement, it has some issues. First of all, it requires special steps to install. The graphite gasket is installed between two flanges, which are fixed by bolts. In order to seal under high fluid pressure, the required bolting torque is high. Secondly, it is laborious to maintain the device. While taking down the device after the experiments, I found the graphite usually sticks to the surface of the flanges. It is important to have a clean contact surface between the metal and the gasket, therefore I need to remove all the remainder which is still stuck to the mental surface. The graphite gasket is not reusable, it is good for one test. On the other hand, rubber o-rings and metallic seal are reusable.
Figure 5-6: Sealing Material: a) Metallic Seal. b) Graphite Gasket. c) Rubber O-ring.

Figure 5-7: Bolting sequence:
5.4 Procedures for Setting up the Experiment

This section describes procedures for setting up for hydrothermal test using second generation reactor. A itemized list for each step is included in the Appendix A.

There are several things that I need to point out. First, bolting is separated to four phases. The torque applied to the bolts is increased gradually to apply stress evenly. In phase I to phase III of the appendix A, a diametrically opposed sequence (Fig. 5-7) is used to prevent stress relaxation of the bolts. Phase IV is followed to ensure that all bolts have been evenly stressed.

Secondly, the contact surface between the metal and the graphite gasket must be cleaned after each use and before the setting up the test. I use a #150 sand paper to polish the metal surface. As a rule of thumb, the thickness of a graphite gasket should be as thin as possible. A thicker graphite gasket is more likely to have relaxation problem, and leaks in long run. However, a thin one may have less relaxation problem but it may not cover the rough and uneven surface, and leaks in short time.
Chapter 6

Results

This chapter presents the results of mineral composition for hydrothermally reacted GoM-EI material. The conditions and experimental setup for the reacted GoM-EI are listed in Chapter 5. GoM-EI post-test samples have displayed color change due to smectite-to-illite transformation. Color change provides an estimation of the degree of the illitization.

This chapter also covers clay mineral identification of GoM-EI sample by peak position using XRD. If $K^+$-saturated post-test sample is not $Ca^{2+}$ substituted, the dehydrated smectite 001 peak overlaps with illite 001 peak. So proper treatments such as $Ca^{2+}$ substitution and ethylene glycol solvation for post-test or cooked sample are very important for both qualitative and qualitative analysis.

The quantitative analysis was done by Dr. Day-Stirrat. He provided a lot of help in analyzing mineral composition. The detail of mineral transformation is discussed in section 6.4.

6.1 Material Process

The GoM-EI material was cored from Gulf of Mexico Eugenie Island block 330. The depth is around 8000 ft. The natural GoM-EI mudrock has 80g/L of sea salt. Because smectite needs $K^+$ seeding to become illite, in order to accelerate the process, so we need to leach out NaCl from the mudrock using dialysis method. This leached El is
the pretest material or original EI as mentioned in the latter sections.

The fluid chemistry changes for testing procedures and analysis. Different salt concentrations for different tests are provided in advance to avoid confusion. In all of the hydrothermal reaction tests, the pretest material was mixed with 3 mol/L of KCl fluid. Samples scanned by Shell and shown in Fig. 6-2, Fig. 6-5, Fig. 6-7 and Fig. 6-8, went through washing out excess KCl, removing impurities such as organic matter, carbonates and iron oxides and saturating with $Ca^{2+}$ cation.

Sample scanned by Macaulay in Fig. 6-3 is the $Na^+$ saturated pretest GoM-EI. It was prepared using filter transfer method. No impurity removal and $Ca^{2+}$ saturation were done to that pretest sample.

Sample scanned in Fig. 6-4 is the $K^+$ saturated pretest GoM-EI. It was immersed in 3mol/L KCl at room temperature for 18 days. Then excess KCl was washed out from this pretest sample. No impurity removal and $Ca^{2+}$ saturation were done to that pretest sample.

Sample scanned in Fig. 6-6 is a sample from hydrothermal reaction test IS01. It was reacted at 200°C with 3mol/L KCl for 18 days. Then excess KCl was wash out from this IS01 sample. No impurity removal and $Ca^{2+}$ saturation were done to that IS01 sample.

Samples scanned by Shell were prepared using filter transfer method and samples (shown in Fig. 6-4 and Fig. 6-6) scanned by me were using glass method as mentioned in chapter 4.

Samples scanned by Shell, Macaulay and me only contain clay fraction. The clay fraction is separated from bulk material using timed sedimentation.

Cooked sample used for TGA tests is from hydrothermal reaction test IS02. It was reacted at 250°C with 3mol/L KCl for 18 days. Then excess KCl was wash out from IS02 sample. IS02 sample was latter air-dried and grinded pass # 100 sieve. Pretest sample for TGA test is the leached EI. No KCl solution is added to it, so it is $Na^+$ saturated pretest GoM-EI sample.
6.2 Visual Comparison

Fig. 6-1 shows pictures of pretest sample and a post-test IS02 sample which was cooked at 250°C for 18 days. The pretest sample which is a highly smectitic material has a brown color, and the texture is smooth. After cooking, the color and texture of GoM-EI mudrock changes. The color of post-test sample provided an estimation of illitization. If the post-test sample undertakes a great degree of illitization, the color is likely to be navy gray. If the post-test sample goes through medium degree of illitization, the color should be pale brown. If the post-test sample has not transformed, the color is still brown. The visual comparison provides a quick estimation of the degree of transformation. For detailed quantitative analysis, we need to rely on the results obtained from XRD analysis.

6.3 Qualitative Analysis on XRD Pattern

X-ray diffraction is the most common technique used to study the characteristics of crystalline material and to determine the mineralogy of finer grain sediments.

The pretest and post-test samples were sent to Shell for XRD analysis. Samples were chemically treated to remove organic materials and carbonates following Jackson (2005). Samples were Ca$^{2+}$ saturated, then the clay fraction (< 2μm) was separated from the bulk. The textured clay slides were prepared using filter transfer method (Chapter 4.3.4). Then clay slides were scanned under air-dried (AD) and ethylene glycolated (EG) condition from 2° to 47° 2θ. The step size is 0.05° 2θ, and acquisition time for each step is long enough to get a smooth and distinctive XRD profile.

6.3.1 Clay Mineral Identification of GoM-EI Pretest

XRD profiles in this thesis were all obtained from oriented clay slide. The oriented sample preparation method forces the clay mineral particles to lie flat. This method diminishes the hk0 peaks and intensifies the 00l diagnostic basal diffraction.
Fig. 6-2 is the XRD pattern for the $\text{Ca}^{2+}$ saturated air-dried pretest sample. According to Bragg's Law (equation 6.1), the 001 peak at $5.8^\circ$ 2$\theta$ corresponds to a basal spacing of 15.5 Å.

$$d = \frac{n\lambda}{2\sin\theta} \quad (6.1)$$

Where $\lambda$ is the wavelength for x-ray source; the wavelength of a copper source equals 1.54Å; the wavelength of a cobalt source equals 1.79Å. For 001 peak, n equals 1; for 002 peak, n equal 2 and this applies to higher 00l peaks. $d$ is the basal spacing or d-spacing of the clay mineral. $\theta$ is the scattering angle. A list of diagnostic 00l peaks for mineral identification is shown in Table 6.1 (USGS Open Report).

<table>
<thead>
<tr>
<th></th>
<th>2$\theta$ ($^\circ$)</th>
<th>d-spacing (Å)</th>
<th>00l peak</th>
<th>Cation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smectite</td>
<td>5.8</td>
<td>15.2</td>
<td>001</td>
<td>$\text{Ca}^{2+}$ AD</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>12.3</td>
<td>001</td>
<td>$K^+$ AD</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>17.0</td>
<td>001</td>
<td>$K^+$ EG</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>17.0</td>
<td>001</td>
<td>$\text{Ca}^{2+}$ EG</td>
</tr>
<tr>
<td>Illite</td>
<td>8.7</td>
<td>10.1</td>
<td>001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.5</td>
<td>10.1</td>
<td>002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26.5</td>
<td>10.1</td>
<td>003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45.5</td>
<td>10.1</td>
<td>005</td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>12.4</td>
<td>7.1</td>
<td>001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>7.1</td>
<td>002</td>
<td></td>
</tr>
<tr>
<td>Chlorite</td>
<td>6.2</td>
<td>14.2</td>
<td>001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.4</td>
<td>14.2</td>
<td>002</td>
<td></td>
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<td></td>
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<td>004</td>
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</tr>
<tr>
<td>CoK$\alpha$</td>
<td>7.2</td>
<td>14.2</td>
<td>001</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1: 00l Peak Positions for Clay Minerals

The basal spacing of smectite in air-dried state (40% R.H) is around 15 Å. The basal spacing of smectite varies with humidity from 12 to 15 Å in air-dried state. So a peak around $6^\circ$ indicates the existence of smectite. The 001 peak at $8.7^\circ$, which is 10.1 Å, indicates the existence of illite. The peak at $17.5^\circ$ is the 002 peak for illite.

There is a challenge to differentiate between kaolinite and chlorite. Kaolinite mineral has a basal spacing 7.1 Å, and the chlorite mineral has a basal spacing of 14.2 Å. The 002($12.4^\circ$) and 004($25^\circ$) peaks of chlorite overlap the 001($12.5^\circ$) and 002($25^\circ$) peaks of kaolinite (shown in Fig. 6-2 and Fig. 6-8). The 001($6.2^\circ$) peak of
chlorite is masked by the shoulder of smectite 001 peak because the smectite content outnumbers chlorite content a lot and the smectite peak is very broad (Fig. 6-2).

Heating the oriented clay slide to 300°C for one hour collapses smectite 001 peak and reveals the chlorite 001 peak if there is any chlorite in the sample. The Fig. 6-3 proofs the existence of chlorite in the pretest sample. For the heated sample (red curve), the smectite 001 peak disappears, and there is a small peak at 7.2° which corresponds to a basal spacing of 14.2 Å.

The XRD pattern was scanned by Macaulay Scientific Consulting LTD using a cobalt source. Because the x-ray is generated from a cobalt source, the chlorite 001 peak position is different from a copper source 001 peak at 6.2°. Only the XRD patterns in Fig. 6-3 are scanned by a cobalt source, the rest of XRD patterns in this chapter are scanned by a copper source.

6.3.2 The Effect of $K^+$ Cation on XRD Pattern

Processing the material correctly is very important. It is especially true for the study of smectite-to-illite transformation. Illite and smectite have similar structure. When smectite is dehydrated, the d-spacing of smectite is close to that of illite. Additionally, in a sedimentary rock, the smectite is usually Na saturated. Rarely the case will the smectite be $K^+$-saturated. In the hydrothermal test, mudrock is manually dosed with $K^+$. $K^+$ dosing and hydrothermal reaction cause false identification of clay minerals if sample is not properly pretreated.

Fig. 6-5 provides an example for $Ca^+$ saturated pretest GoM-EI. The smectite peak in both air-dried and glycolated condition is relatively sharp and distinctive. The Sample in Fig. 6-4 is $K^+$-saturated pretest GoM-EI. In Fig.6-4, the smectite 001 peak is at 7.2°. This means the $K^+$ cation reduces the smectite basal spacing to 12.3Å. On the other hand, illite 001 peak intensity in air-dried state is elevated by four times comparing with the glycolated $K^+$ saturated pretest GoM-EI. Under the assumption that there is no smectite-to-illite transformation in room temperature, the elevated illite 001 peak indicates that $K^+$ also reduces some portion of smectite basal spacing to 10Å. The 10Å dehydrated smectite peak overlaps illite 001 peak, and
it increases the peak intensity at 8.7° drastically. The EG XRD profile in Fig. 6-4 only has one sharp peak at 5.2 and the illite intensity drops to normal. This means ethylene glycol has expanded the 12.3Å smectite and 10 Å smectite to 17 Å.

How does the $K^+$ saturation affect the hydrothermal altered post-test GoM-EI sample? The IS01 sample was cooked at 200°C with 3mol/L KCl solution for 18 days. From quantitative analysis by Dr. Day-Stirrat, we know the IS01 sample has 43% discrete smectite. Fig. 6-7 provides an example for $Ca^+$ saturated post-test IS01 GoM-EI. The smectite peak in air-dried condition is very board, the right shoulder of smectite 001 peak and the left shoulder of illite 001 peak connects. It means that smectite has several hydration states i.e. 10Å, 12Å and 15Å, resulting a diffused smectite 001 peak. EG treatment replaces water molecule with EG molecule, thus unifies the smectite basal spacing to 17Å as shown in Fig.6-7 the green curve. Sample in Fig. 6-6 is $K^+$ saturated post-test IS01 GoM-EI. In the air-dried condition, the $K^+$-smectite peak does not exist. Instead of a portion of smectite, all of the smectite basal spacing reduces to 10Å. The EG treatment does not expand the dehydrated smectite to 17 Å as what happen in Fig.6-7. Under the influence of heating and $K^+$ dosing, the XRD patterns for both air-dried and EG condition display no smectite peak. It is very deceiving to conclude that the sample has no smectite because smectite is dehydrated.

The proper technique to treat the hydrothermal altered $K^+$ GoM-EI material involves cation saturation with bivalent cation $Ca^{2+}$ and to solvate the sample in ethylene glycol.

### 6.3.3 Qualitative Results based on Peak Intensity

Fig.6-8 summarizes the oriented XRD pattern under $Ca^{2+}$ saturated and EG condition. The XRD pattern were recorded from 2° to 47° 2θ angle. Major peaks in the Fig. 6-8 are labeled. S stands for smectite, I stands for illite, K stands for kaolinite and Cl for chlorite.

For pretest sample which is represented by blue line, the intensity for smectite 001 peak at 5.2° is high, indicating the material is highly smectitic. Peaks at 8.7°, 17.5°,
26.5° and 46° are from illite. Kaolinite and chlorite peaks share the same location at 12.4° and 25°.

The intensity of the smectite 001 peak reduces as the temperature increases. When temperature is higher than 225°C, the smectite 001 peak completely disappears; this indicates the discrete smectite is almost zero for samples cooked at a temperature that is higher than 225°C.

The intensity of shared peaks at 12.4° and 25° reduces as the temperature increases. When the temperature is higher than 200°, both peaks diminish to almost zero. So the 250°C, 300°C and 300°C 29d samples are expected to have little amount of kaolinite and chlorite. The intensity of illite 001 peak at 8.7° increases as the temperature increases, in the meantime, the width of the illite peaks at 9°, 18° and 47° is increasing. Those changes indicate that the illite content is increasing but illite is not well crystallized. In general, if a peak is wide, it means that the number of layers (N) in a clay particle is small. The peak of a well-crystallized mineral is sharp.

6.4 Quantitative Results of Transformed Samples

Quantitative analysis of GoM-EI samples were conducted by Dr. Day-Stirrat using a computer software called Newmode II. The Newmode II software utilizes the Rietveld method that minimizes the weighted sum of square of the difference between the experimental XRD pattern and the calculated XRD profile, and determines the weight fraction of each clay mineral phase.

Fig. 6-9 summarizes the mineral composition for the cooked material and pretest material. The pretest material has 13% of discrete illite, 31% of mixed-layer phase or I/S phase, 43% of discrete smectite, 9% of kaolinite and 4% of chlorite. If we look at the 18-day tests (the first seven column in Fig. 6-9), we see a trend that discrete smectite reduces as the temperature increases, the number drops from 43% to 0%. The I/S phase increases from 31% to 96%. The discrete illite percentage also drops, but the trend is relatively flat compared to discrete smectite. The number fluctuates up and down before 250 °C, then at 300 °C, discrete illite drops to 3 %. In the first
stage of smectite-to-illite transformation, the discrete smectite and discrete illite are represented by random ordered mixed layered I/S phase. As the reaction continues, random ordered I/S phase transforms to ordered I/S phase. In the final stage of the transformation, illite content in the I/S phase continues to increase and finally it becomes a discrete phase. It is observed in the 300°C 29 days sample (the last column of Fig. 6-9), the percentage of discrete illite bounces back to 9.5% when the illite% in the I/S phase is reaching almost 100%. Fig. 6-10 shows the illite and smectite percentage in the mixed layer phase. As the temperature increases, the illite curve follows an increasing trend whereas smectite content decreases.

There are some discrepancies with respect to the general trend. For 225°C sample, the discrete illite increased to 24% very rapidly. There could have been some segregation of material in the batching. Alternatively, the discrete illite and I/S are quite similar in terms of diffraction pattern. But in terms of the general smectite trend (Fig. 6-11), where total smectite is the sum of discrete smectite and smectite in the I/S phase, the total smectite% is perfectly on trend. The figure 6-11 shows that total smectite decreases monotonically as the temperature increase. To note, in the 175C sample, the discrete smectite is zero and a smectite rich I/S which is S/I in this case is added to reduce the number of phases in the XRD pattern modeling.

6.5 Is Smectite-to-illite Transformation Releasing Water?

In the previous section, the XRD analysis confirmed that I have successfully transform smectite to illite. According to the transformation theory, the interlayer water is released from interlayer space during the transformation. In order to measure the amount of the released interlayer water, thermal gravimetric analysis (TGA) was used determine the water loss. Dr. Simone Musso from Schlumberger ran TGA tests on pretest material and IS02 (200°C 18days) sample. TGA records the weight of a sample continuously as the temperature increases. The temperature increasing rate
is 20 °C/min for both samples. In terms of sample preparation for both samples, the excess cation in the pore fluid is leached out. Then the slurry is air dried and hand grinded passing #100 sieve.

The Fig.6-12 a) and b) are obtained from pretest sample and IS02 sample respectively. The blue curves represent the weight change as a function of temperature. The orange dash lines are the derivative of weight change with respect to temperature. The pretest sample loses 2.65% of mass from 0 to 300 °C, whereas the IS02 sample only 0.56%. The 0 to 300°C is the window for dehydration during which the water adsorbed on clay surfaces and the water inside the interlayer space evaporates. The adsorbed water is negligible for air dried powder in low relative humidity. The loss of interlayer water in the smectite is the major reason for weight change. We can use TGA to measure the interlayer water loss. Alternatively, we can calculate the interlayer water mass using XRD result. The total smectite for pretest material and IS02 are 50.4% and 15.3% respectively. The weight percentage of interlayer water in the smectite at 40% relative humidity is 9.5% (Sposito and Prost, 1982). Both samples have 63 wt% of clay. Then the weight of interlayer water in the sample equals the multiplication of total smectite%, mass% of interlayer water in smectite, and clay % in the whole sample. The calculated results show pretest material has 3.02% of interlayer water, and IS02 sample has 0.92 % of interlayer water. The difference of weight change using TGA data matches well with the interlayer water weight change using XRD data. This confirms that the smectite is releasing interlayer water when it transforms to illite.

<table>
<thead>
<tr>
<th>TGA</th>
<th>XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehydration Loss%</td>
<td>Total Smectite%</td>
</tr>
<tr>
<td>GoM-EI Pretest</td>
<td>2.65</td>
</tr>
<tr>
<td>IS02 250°C</td>
<td>0.56</td>
</tr>
<tr>
<td>Difference</td>
<td>2.09</td>
</tr>
</tbody>
</table>

Table 6.2: Water Loss Calculation
Figure 6-1: Visual Comparison of Pretest Sample and Post-test Sample

Figure 6-2: Diagnostic XRD Pattern for $Ca^{2+}$ Saturated Air-dried Pretest Sample (Scanned by Shell)
Figure 6-3: XRD Pattern for Na$^+$-Pretest Sample. The heated XRD pattern shows the chlorite peak at 7.2° when smectite peak collapses due to heating (Scanned by Macaulay Scientific Consulting LTD).

Figure 6-4: XRD Pattern for K$^+$ Saturated Pretest Sample
Figure 6-5: XRD Pattern for $Cu^{2+}$ Saturated Pretest Sample (Scanned by Shell)

Figure 6-6: XRD Pattern for $K^+$-saturated IS01
Figure 6-7: XRD Pattern for $Ca^{2+}$-saturated IS01 (Scanned by Shell)
Figure 6-8: XRD Pattern Summary of Pretest Sample and Post-test Samples. Samples were scanned in Ca$^{2+}$-saturated EG condition by Shell.
Figure 6-9: Clay Mineral Composition of Pretest Sample and Post-test Samples (Analyzed by Dr. Day-Stirrat)
Figure 6-10: Illite% and Smectite% in the Mixed-layered Phase of Pretest Sample and Post-test Samples (Analyzed by Dr. Day-Stirrat)

Figure 6-11: Total Smectite% Summary of Pretest Sample and Post-test Samples
Figure 6-12: TGA Data for Pretest Sample and IS02 Sample
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Appendix A

Procedures for Setting up the Experiment

This section describes procedures for setting up for a hydrothermal test using the second generation reactor.

1. Weigh 30 g of leached GoM-EI powder

2. Mix the powder with 3 mol/L KCl solution to achieve a water content of 87%

3. Fill the first ceramic cup with slurry then put the cup into the reactor

4. Pour in KCl solution to the top of the first cup then cover the cup with a porous stone

5. Repeat step 3 with the second cup and place it on top of the first one

6. Place one graphite gasket on the lip of the bottom part of the reactor

7. Assemble the top part of the reactor and install the bolts, tighten them by hand, make sure gasket is centered

   Note: Bolts and washers should be lubricated with anti-seize compound in advance
8. Fix the reactor in a vise, use a torque reading wrench to tighten bolts to 80 Nm in three phases
   Phase I: Torque bolts up to 30% of the final torque following the diametrically opposed sequence specified in Fig. A-1
   Phase II: Repeat phase I, increasing the torque to 60% of the final torque value
   Phase III: Repeat phase II, increasing the torque value to the final torque value
   Phase IV: A final tightening should be performed following an adjacent bolt-to-bolt sequence to ensure that all bolts have been evenly stressed

9. Fill the reactor with fluid to minimize entrapped air, connect the reactor to pressure-volume actuator (PVA) with copper tube

10. Pressure up the reactor to desired cell pressure using manual control

11. Switch to automatic control and check to see if there is a leak

12. If no leak is found, depressurize the reactor, adjust the piston position, make sure there is enough space for piston to backup to compensate the volume expansion of water during heating

13. Attach the heating ring to the reactor, then close the valve and turn on temperature control, adjust the value to desired value on the panel

14. The pressure control should stay off, until the pressure increased by water volume expansion reaches the target test cell pressure. Then let automatic control take over the piston movement.

15. It is important to leave the piston with enough stroke. Piston will continually back off until the target temperature is reached.

16. Set data recording rate to 4 minutes per reading for both pressure transducer and displacement transducer
References


flow related to a large growth fault, south eugene island block 330 field, offshore louisiana. *AAPG bulletin*, 83(2), 244–276.


