Fourier Transform Infrared Spectroscopic Studies of Clay and Shales

Katti, Kalpana S.
University Distinguished Professor
e-mail: Kalpana.Katti@Ndsu.Edu

Katti, Dinesh R.
Professor
e-mail: Dinesh.Katti@Ndsu.Edu

Department of Civil Engineering, North Dakota State University, Fargo, ND, USA

ABSTRACT

Fourier transform infrared spectroscopy (FTIR) technique is a powerful non-destructive technique that is used to study molecular interactions in a variety of materials. This technique is used to investigate the molecular interactions in geomaterials such as swelling clays and oil shales. This technique was used to study molecular interactions during swelling of expansive clay, interaction of swelling clay and fluids with various dielectric constants and mineral-kerogen interactions in oil shales. This research provides an insight into molecular interactions and their role on meso and macroscale properties of these geomaterials. This understanding is essential for geomaterials where molecular interactions play important role in influencing macroscale properties. An overview of our research on geomaterials using FTIR is presented in this paper.

1. INTRODUCTION

In geotechnical engineering, geo-environmental engineering and petroleum engineering, the interactions between mineral and fluids play a vital role on the macroscopic properties of clays and shales. The macroscale response of these materials is a multiscale behavior that is hierarchically related to meso, micro and molecular or nanoscale behavior. Accurate experimental techniques to evaluate nature of molecular interactions are necessary to bridge the molecular behavior to meso and macroscale responses such as swelling, swelling pressure, permeability and load deformation response. An experimental technique that can be used with undisturbed samples of these geomaterials is necessary. Fourier transform infrared spectroscopy is a nondestructive technique used for evaluating molecular interactions in a variety of material systems and phases. This technique involves an incident infrared signal on the sample that interacts with material of the sample and a transmitted or reflected beam of infrared light is collected by a detector. The interaction between infrared light and sample leads to vibration of bonds in the materials leading to absorption of characteristic energies in the detected beam. The transmitted or reflected beam is thus a molecular signature of the material of the sample and indicates vibrational modes for all the bonds in the material. In our previous work, we have extensively used FTIR technique for biological and synthetic nanomaterials to elucidate the role of molecular interactions on macroscale properties (Bhowmik et al., 2007; Katti et al., 2010; Katti et al., 2008; Mohanty et al., 2008; Sikdar et al., 2009; Verma et al., 2008; Verma et al., 2006a, b, 2007). We have used this technique to evaluate the changes in interactions of molecules and clay platelet orientations with addition of water. These changes in molecular interactions are then related to swelling and swelling pressure in montmorillonite clays. Using innovative experiments with the FTIR, for the first time the flow rate of water in the clay interlayer has been found. This technique was also extensively used to evaluate the nature of interactions between clays and solvents of varying dielectric properties present in leachates from landfills. The spectroscopic technique is also used to study interactions between kerogen, the precursor to crude oil, and minerals in oil shales. In this paper, we will provide an overview of the use of this powerful technique for geotechnical, geo-environmental and petroleum engineering applications.

2. MATERIALS AND METHODS

Na-montmorillonite (Swy-2, Crook County, Wyoming) of cationic exchange capacity 76.4 mequiv/100 g was obtained from the Clay Minerals Repository at the University of Missouri, Columbia, MO. The Swy-2 montmorillonite has the chemical formula NaSi_16(Al,Fe,Mg)O_20(OH)_4. Deionized water was used for water-clay experiments. In preparation of Na-montmorillonite (MMT)-organic fluid complexes, 90-100% purity Formamide, 99.9% purity acetone 99.7% purity toluene and 99.9% purity trichloroethylene were obtained from Mallinckrodt Baker, Inc. NJ, 99.9% purity chloroform.
was obtained from EMD Chemicals Inc. NJ and 99.9% purity methanol was obtained from Alfa Aesar, MA.

The oil shale samples are from the green river formation in Colorado, USA. The core section is seven feet long and is obtained from a depth of 560 – 572 ft below the Earth’s surface. Each core contained dark and light colored regions at various locations. IR spectroscopic experiments were conducted using Nicolet 850 FTIR spectrometer with KBr beam splitter in the range of 4000-400 cm$^{-1}$ at a spectral resolution of 4 cm$^{-1}$. Time dependent XRD experiments were performed using X-ray diffractometer, model D8 Discover (Bruker AXS), in the range of 4° to 10° and at a scanning rate of 2° degree per minute. Consecutive XRD patterns of the clay-water slurry were acquired without having any relapse time. X-ray diffraction experiments that were conducted to find the $d_{(001)}$ spacing of clay with different water contents were performed using X-ray diffractometer, model Philips X’pert, Almelo, Netherlands, equipped with secondary monochromator and Cu-tube using CuKα radiation of wavelength 1.54056 Å. The rate of scan was 2° degree per minute and the scan range was from 2° to 10°.

3. RESULTS

Clay-water Interactions and Flow Rate of Fluid in Na-Montmorillonite Interlayer

We have studied the clay-water interactions in Na montmorillonite with respect to swelling and swelling pressure (Katti and Katti, 2006). FTIR experiments were conducted on undisturbed swelled samples of saturated clay at various amounts of swelling, 0%, 25%, 50% and 75% swelling using a controlled uniaxial swelling cell (CUS) (Katti and Shanmugasundaram, 2001). Using micro attenuated total reflectance spectroscopy, it was found that the clay particles are most oriented at 0% swelling and the misorientation of clay particles increases with the increase of swelling when the clay is subjected to controlled swelling.

Extensive studies were conducted using FTIR, XRD and atomic force microscopy to evaluate the flow rate of water in the interlayer of Na-montmorillonite clay and to evaluate the interactions between clay and water (Amarasinghe et al., 2008). Clay-water slurry samples were prepared and immediately placed in the FTIR and XRD instruments. In FTIR, we specifically studied the evolution of O-H stretching vibration, H-O-H bending vibration and Si-O stretching vibration regions of the $p$ and $s$ polarized IR spectra with time. d-spacing versus time data was obtained from XRD experiment. The H-O-H bending vibration band shifts towards lower energy of 1634 cm$^{-1}$ from 1694 cm$^{-1}$ with increasing clay-water interaction time, as shown in figure 1. As the water in the pores of the clay flows into the clay interlayer, H-O-H bending vibration becomes weaker while the O-H stretching vibration becomes stronger. It appears that a reduced degree of freedom for interlayer water molecules that are hydrogen bonded to the surface oxygen of the clay sheets, for bending causes the H-O-H bending vibrations to weaken. Two stages of shift in the H-O-H bending band with respect to clay-water interaction time are observed. In the first stage of the shift, the band shifts to lower energy by 60 cm$^{-1}$ in about 25 minutes. We attribute this shift to bulk water (in the pore spaces) entering into the clay interlayer. The O-H bending band stabilizes at 1634 cm$^{-1}$ position for some time before the second stage of shift of about 5 cm$^{-1}$, occurs. The second stage of shift is attributed to the loss of water molecules in the interlayer water from the sample. During this period, some of the loosely bound water molecules are released from the clay interlayer leaving fewer number of water molecules in the interlayer. These water molecules in the interlayer now have more opportunity to make H bonds with surface oxygen which reduces the freedom of H-O-H bending, thus resulting in shift of H-O-H bending band to lower energy.

Fig. 1: FTIR Spectra ($p$ Polarized Reflectance) Showing the Change of O-H Stretching of Bulk Water (Around 1700 cm$^{-1}$) to Structural Water (Around 1633 cm$^{-1}$) with Increasing Clay-Water Interaction Time (Amarasinghe et al., 2008)

Fig. 2: Change in Band Position of H-O-H Bending Vibration, with Increasing Clay-Water Interaction Time (Amarasinghe et al., 2008).
Next, based on the interaction time obtained from FTIR, d-spacing for that time from XRD and platelet size from atomic force microscopy phase imaging, the velocity of water molecules in the interlayer was found to be $3.22 \times 10^{-9}$ cm/sec.

**Nature of Clay-Fluid Interactions**

The nature of clay fluid interactions with fluids ranging from highly polar fluid, formamide to nonpolar fluid toluene are found using FTIR as shown in figure 3.

Seven different fluids with varying dielectric constant values ranging from 110 to 2.4 were used. Since water molecules are relatively least constrained molecules in the clay interlayer, any changes in the vibration of these water molecules are indicatives of influence of organic molecules on the interlayer. Characteristic H-O-H bending vibration of water, is studied using FTIR spectroscopy. Changes in the clay molecular structure were studied by evaluating Si-O stretching vibration, which is also an indicator of influence of organic fluids on the clay structure. A good correlation between dielectric constant and change in the H-O-H bending vibration of interlayer water was observed as shown in Figure 4.

**Mineral-Kerogen Interactions in Oil Shales**

Oil shales are sedimentary rocks that contain minerals, kerogen, and bitumen that have a potential to yield a significant amount of oil from kerogen, a precursor to crude oil. Recent techniques to extract “oil” from oil shale are via pyrolysis or the chemical decomposition. However, due to high input energy costs and detrimental effect of these processes on the environment, effective extract of oil from oil shale is a challenge. Fundamental research to understand mineral-kerogen interactions in oil shales is undertaken using experimental and modeling techniques. A picture of the green...
The river core sample used in the study is shown in figure 5. Light and dark colored regions were observed in the sample. FTIR spectra are obtained from the two regions and compared as shown in figure 6.

The FTIR results revealed compositional differences in the light and dark regions with more kerogen rich regions in the light samples and a strong indication of mineral-kerogen interactions in the light samples.

4. CONCLUSIONS

FTIR spectroscopy is a powerful technique to evaluate the nature of molecular interactions in geomaterials that allows for relating molecular scale interactions to the bulk properties of these materials. We have shown the innovative use of this technique for clays and oil shales.

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REFERENCES


