FT-IR Study of CO₂ Interaction with Na⁺ exchanged Montmorillonite

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ABSTRACT

Carbon capture, utilization and storage (CCUS) in saline reservoirs in sedimentary formations has the potential to reduce the impact of fossil fuel combustion on climate change by reducing CO₂ emissions to the atmosphere and storing the CO₂ in geologic formations in perpetuity. At pressure and temperature (PT) conditions relevant to CCUS, CO₂ is less dense than the pre-existing brine in the formation, and the more buoyant CO₂ will migrate to the top of the formation where it will be in contact with cap rock. Interactions between clay-rich shale cap rocks and CO₂ are poorly understood at PT conditions appropriate for CCUS in saline formations. In this study, the interaction of CO₂ with clay minerals in the cap rock overlying a saline formation has been examined using Na⁺ exchanged montmorillonite (Mt) (Na⁺-STx-1) (Na⁺Mt) as an analog for clay-rich shale. Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR -FTIR) was used to discern mechanistic information for CO₂ interaction with hydrated (both one- and two-water layers) and relatively dehydrated (both dehydrated layers and one-water layers) Na⁺-STx-1 at 35°C and 50°C and CO₂ pressure from 0-5.9 MPa. CO₂-induced perturbations associated with the water layer and Na⁺-STx-1 vibrational modes such as AlAlOH and AlMgOH were examined. Data indicate that CO₂ is preferentially incorporated into the interlayer space, with relatively dehydrated Na⁺-STx-1 capable of incorporating more CO₂ compared to hydrated Na⁺-STx-1. Spectroscopic data provide no evidence of formation of carbonate minerals or the interaction of CO₂ with sodium cations in the Na⁺-STx-1 structure.

1. Introduction

Climate change, commonly referred to in the popular media as global warming, is a significant environmental challenge (IPCC, 2005). During the last half century, the increase in concentration of CO₂ in the atmosphere has paralleled increases in global average temperature, and the U.S. National Climate Assessment released in May 2014 reports that weather related disasters such as droughts, flooding, and severe storms are likely to be exacerbated by global warming. As a result, there has been much discussion concerning methods to reduce anthropogenic CO₂ emissions. These range from overall energy conservation, to reducing our dependence on fossil fuels, to developing methodologies to reduce CO₂ emissions to the atmosphere produced by burning of fossil fuels.

Carbon capture, utilization, and storage (CCUS) is a method whereby CO₂ is captured at the location where it is generated (i.e., a fossil-fuel burning power plant) and the CO₂ is stored or sequestered in a manner that prevents its introduction into the atmosphere (McConnell, 2012). One CCUS option that holds great promise involves injection of the CO₂ as a supercritical phase into the geologic subsurface where it can be held permanently (Herzog, 2001). Geological formations that have been proposed for CCUS include deep saline formations, depleted oil and gas reservoirs, unmineable coal seams, organic-rich shales, and basalts (US-DOE-NETL, 2012).

During the initial stages of the injection when structural and stratigraphic trapping dominate, the more buoyant supercritical CO₂ phase will tend to rise and accumulate at the top of the permeable formation, beneath the impermeable confining layer (Figure 1). In many sedimentary basins containing deep, saline formations that might be accessed for CCUS, an effective and common cap rock is shale or mudstone, which can contain significant quantities of

various types of clay minerals (Shaw and Weaver, 1965; Benson, 2008). Depending on the physical properties of the shale, the accumulated CO₂ may interact with minerals in the confining unit.

The smectites which includes Mt is a group of clay minerals commonly found in shale caprock.. Smectites have a structure composed of stacked layers formed by bonding of two tetrahedral sheets to an individual octahedral sheet. These 2:1 layers have a net negative charge, which is balanced by cations that occupy the interlayer space, as shown in Figure 2 (Myshakin et al., 2013). This net negative charge results from cation substitutions either in the tetrahedral sheets or in the octahedral sheets of the 2:1 layer. The distribution of the charge within the 2:1 layers impacts the interactions of interlayer space ions with the silicate framework. The layer charge for idealized Mt originates within the octahedral sheet, but natural samples of Mt typically have some degree of tetrahedral charge. Smectites are referred to as “swelling clay minerals” because of the tendency for polar fluids (typically water) to be taken up in the interlayer space, causing the structure to expand (Yamada et al., 1994). The distance of adjacent 2:1 layers (d_{001} value) depends upon the amount of H₂O incorporated in the interlayer space (i.e., it is directly related to the hydration state of the clay mineral); furthermore, the water content in the interlayer space is impacted by the activity of water (e.g., relative humidity) in contact with the mineral. The conventional terminology that has been developed to describe the amount of water in the interlayer space refers to completely dehydrated clay minerals, and those that contain one, two, or three water layers. However, samples with partially hydrated layers may also occur.. The d_{001} value for dehydrated Mt is ~10 Å; for a one water layer state of hydrate, the value is ~12.4 Å; and for a two water layer state of hydration, the value is ~15.2 Å (Yamada et

al., 1994). Thus, the molar volume of smectite may increase by ~20-50% as water enters the interlayer space upon hydration.

Understanding how the introduction of CO₂ into a saline formation alters the physical and chemical properties of shale cap rock containing minerals like Mt is necessary to have confidence that a shale seal has the necessary integrity for long term storage. Busch et al. (2008) examined CO₂ interactions with a clay-containing shale (the Muderong shale) and with several clay mineral standards, including Mt STx-1 and SWy-2. Their results show that CO₂ diffusion through the formation after injection was slowed by the low permeability and expansive properties of the smectites. They also found that CO₂ adsorption/absorption on smectite could be significant, increasing with dehydration of the clay mineral. They concluded that the seal quality would be enhanced as a result of interaction of CO₂ with the overlying shale. De Pablo et al. (2007) predicted the hydration state of Ca⁺⁺ Mt at typical sequestration depths based on Monte Carlo simulations; they predict that the clay mineral would maintain a one water layer of state of hydration at temperature and pressure conditions of typical storage reservoirs.

Previous studies have been applied infrared spectroscopy and X-ray diffraction (XRD) to examine CO₂ interactions within the interlayer space of Mt. Fripiat et al. (1974) demonstrated that CO₂ intercalates into the interlayer space of dehydrated, ion-exchanged Mt at low temperatures based on XRD and infrared absorption analyses. Using a Mt that exhibited some tetrahedral charge, they found a dichroic effect implying that CO₂ can orient in the interlayer space (i.e., is at least partially restrained rotationally), with the strength of the effect dependent on the type of interlayer space cation. Further, they found that CO₂ intercalation into dehydrated smectite results in layer expansion, with d_{001} value expanding from 10.0 Å to 12.3 Å for Na⁺-Mt clay mineral exposed to 700 torr CO₂ at -48°C. This latter result has been demonstrated at PT

conditions relevant to CCUS with direct evidence by Rother et al. (2013) based on neutron diffraction analyses and by Loring et al. (2012) using XRD, MAS NMR, and *in situ* high pressure ATR-IR on ion-exchanged versions of Mt STx-1 with less than one monolayer of hydration in the interlayer space. Rother et al. (2013) used a sodium-exchanged sample (Na^+ -STx-1) and Loring et al. (2012) used a calcium exchanged sample (Ca^{++} -STx-1). Approximately 70–80% of the layer charge for STx-1 derives from the octahedral sheet, based on analysis of Mg exchange data in Van Olphen and Fripiat (1979) and Jaynes and Bigham (1987). Schaefer et al. (2012) determined that exposure of one water layer Ca-STx-1 to anhydrous supercritical CO_2 does not displace the interlayer water but expands the interlayer space. However, when two water layer Ca-STx-1 is exposed to anhydrous supercritical CO_2 , the interlayer space is dehydrated causing the sample volume to shrink. Schaefer et al. (2012) concluded that CO_2 does interact with Ca-STx-1 and that the extent of the interactions depends largely on the initial hydration state of the clay mineral. Similarly, Giosting et al. (2012) showed that Na^+ -exchanged SWy-2 (Na^+ -SWy-2) swells in the presence of CO_2 and the amount of swelling is dependent upon the initial hydration state.

Cygan et al. (2010) examined the molecular interactions associated with CO_2 intercalation into Mt with H_2O based on molecular dynamics simulations and suggested that CO_2 is confined in the interlayer space. More recently, Myshakin et al. (2013) conducted molecular dynamics simulations of CO_2 intercalation in hydrated Na^+ -Mt using a turbostratically stacked model for the clay mineral framework (which more accurately reflects the structure of clay minerals samples in the lab). They found that interlayer space Na^+ ions are displaced into the centers of hexagonal rings of silica tetrahedra linked by shared oxygens, and that the occupancy by Na^+ increases with increasing $\text{CO}_2/\text{H}_2\text{O}$ in the fluid. In the simulations by Myshakin et al.

(2013) the Mt was not open to a fluid reservoir (i.e., the simulations did not explore CO₂-H₂O equilibrium between an interlayer space and free fluids); rather the study focused on the interlayer space structure for given amounts of CO₂-H₂O.

In summary, results of several experimental and computational studies indicate that CO₂ enters the interlayer space for both Na⁺ and Ca⁺⁺ exchanged Mt, with the details depending on the initial hydration state of the clay mineral.

In this study, infrared spectroscopy was applied to further understand the mechanism associated with interactions between CO₂ and Mt, using the sample described by Rother et al. (2013) (Na⁺-STx-1). As noted, Rother et al. (2013) used observations from excess adsorption and neutron diffraction to show that when CO₂ entered the interlayer space of Na⁺-STx-1, water was not displaced at the sub-single water layer coverage. These researchers recommended that future research should include spectroscopic measurements to discern the binding sites of CO₂ and water molecules. Other studies have also recommended vibrational spectroscopic studies to further discern the interaction with CO₂ and Mt under a broad range of conditions. (Giosting et al., 2012). Objectives of this study are 1) to define the mechanism for CO₂ interaction with Na⁺-STx-1 and 2) to understand the role of water in the Na⁺-STx-1 interlayer space. Specifically, hydrated and relatively dehydrated Na⁺-STx-1 were exposed to anhydrous CO₂ and monitored with Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) to discern mechanistic information for CO₂ interaction with the Na⁺-STx-1 and examine any CO₂-induced perturbations in vibrational modes associated with interlayer water or the silicate framework. The interaction of CO₂ with Na-STx-1 was investigated at pressures up to 5.9 MPa, a range that lies between CO₂ pressures of <120 torr (<0.016 MPa) (Fripiat et al., 1974) and 9

MPa (Loring et al., 2012; Loring et al., 2014) explored in previous FTIR studies on clay mineral- CO_2 interaction.

2. EXPERIMENTAL SECTION

2.1. Na^+ Mt Sample (Na^+ -STx-1)

In this study, the same Na^+ -exchanged Mt (Na^+ -STx-1) sample characterized by Rother et al. (2013) was used directly for all infrared measurements. Mt STx-1 is a clay mineral standard from the Clay Minerals Society source clay mineral repository. Several detailed chemical analyses of STx-1 have been published (Mermut and Cano, 2001). Determination of its structural formula (and, hence, layer charge distribution) from published chemical analyses is problematic due to inherent impurities that include ~30% opal, even in processed samples (Chipera and Bish, 2001; Mermut and Cano, 2001). However, analysis of Mg-exchange capacity relative to total cation exchange capacity suggests ~70–80% of the layer charge originates in the octahedral sheet (Van Olphen and Fripiat, 1979; Jaynes and Bigham, 1987). The sample was first reacted with 1 M sodium acetate buffer at pH 5 for 2 weeks to remove traces of calcite. The acetate was then removed by dialyzing the clay mineral in deionized water until the wash conductivity was 18 $\text{M}\Omega$ cm. The sedimentation method was used to separate the <2 μm clay mineral fraction. Then, the <2 μm clay mineral fraction suspensions were flocculated by the addition of NaCl (5M). The clay mineral was kept in the NaCl solution for seven days to allow complete exchange with the solution to produce a Na^+ -STx-1. Lastly, the excess salt was removed by dialyzing the suspension in deionized water, followed by freeze-drying.

2.2 Infrared Spectroscopy

All Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR) measurements were collected with a single-beam FTIR spectrometer (Thermo Electron Nexus 4700 FTIR ESP) equipped with a wide-band MCT detector. Unless otherwise noted, 250 scans were collected with an instrument resolution of 2 cm^{-1} over the spectral range extending from 4000 to 600 cm^{-1} .

Infrared spectroscopy experiments at variable pressures were conducted using two custom-designed tunnel ATR (attenuated total reflectance) stainless steel cells from SpectraTech that were connected in tandem via 0.16 cm stainless steel tubing such that each cell experienced the same CO_2 pressure. The cells can accommodate pressures up to 10 MPa . The cells are described in detail by Goodman et al. (2005). A cylindrical zinc selenide (ZnSe) ATR crystal was placed inside each cell. The ATR crystal is 2.8 cm long and 0.6 cm in diameter, the incidence angle with the infrared light source was 45° , and the number of reflections within the crystal was 11. One cell contained a ZnSe ATR crystal with no sample present and the other cell contained a ZnSe ATR crystal coated with $\text{Na}^+\text{-Mt}$. Teflon O-rings were used to establish a high-pressure seal between the stainless steel chamber and ATR crystal. The cells were placed on a manual linear translator inside the FTIR spectrometer such that they could be moved to allow infrared light to probe either the blank ATR crystal or the ATR crystal coated with the sample. Minimum penetration depth of the infrared beam into the sample is estimated to be $\sim 1\text{ }\mu\text{m}$. This ensures that both the bulk and surface of the sample are interrogated during analysis. The cells were enclosed in a thermal jacket that allowed a temperature-controlled fluid to circulate through the external jacket to either heat or cool the cells. The ATR cell assembly was connected to a gas handling system consisting of a syringe pump (ISCO model 260D), a port for gas introduction, and a pressure transducer (OmegaDyne Inc PX01K1-5KGV). The total volume of

the system was estimated to be ~1 ml. Carbon dioxide (99.998% supercritical grade) and ultra-high purity nitrogen (UHP) were used as supplied from Butler gas.

The Na⁺-Mt sample (Na⁺- STx-1) is from the same bulk sample that was studied by Rother et al. (2013). The sample, described later as hydrated Na⁺- STx-1 , was mixed with methanol to form a slurry and a small amount of the slurry (~10 mg) was painted onto one of the ZnSe ATR crystals to form a thin coating. After the methanol evaporated, the Na⁺- STx-1 coated crystal was placed inside the cell and the sample port was sealed. The sample chamber was flushed with ultra-high purity nitrogen before analysis. Desorption (evaporation) of methanol used during sample preparation was verified by the absence of IR absorption bands at 2960, 2844, 1345, and 1033 cm⁻¹ corresponding to methanol peaks (Shimanouchi, 1972). The sample was thermally equilibrated at 35°C by circulating a 50:50 ethylene glycol:water mixture (NESLAB RTE 7) through the temperature jacket. Background spectra were then collected from the cell containing a ZnSe ATR crystal with no sample present and the other cell containing a ZnSe ATR crystal coated with Na⁺- STx-1. The pressure cells were then exposed to 0.5 MPa of CO₂ and then sealed off from the CO₂ source for equilibration. One spectrum was recorded from the cell containing both CO₂ and Na⁺- STx-1 and one spectrum was recorded from the cell containing only CO₂. After the spectra from the two cells were processed, the one for the cell containing only gaseous CO₂ was subtracted from that for the cell with both CO₂ and Na⁺- STx-1 to obtain an absorption spectrum of CO₂ interacting with the Na⁺- STx-1. Carbon dioxide adsorption/absorption was monitored with ATR-FTIR by following the growth of the ν_3 anti-symmetric stretching mode (near 2343 cm⁻¹) and ν_2 bending mode (near 660 cm⁻¹) of CO₂ versus time. Adsorption/absorption is reported when the mechanism is not clear. However, recent work suggests that absorption into the interlayer is the dominant process particularly at lower pressures

below the supercritical point (Schaef et al., 2015). Spectra were collected until the CO₂ adsorption/absorption bands no longer changed with time. Equilibrium was achieved within 15 minutes as evidenced by the fact that there were no spectral changes observed after 15 minutes, although the interaction was monitored for 4 hours. This procedure was repeated by increasing CO₂ pressure to 1.8, 3.1, 4.4, and 5.8 MPa.

The dehydrated Na⁺-STx-1 sample was dried by raising the temperature in the cell to 98°C under N₂ gas flow. Loss of water was determined with ATR-FTIR by monitoring the decrease in the ν_3 anti-symmetric stretching mode and ν_1 symmetric stretching mode bands for adsorbed water between 3560 – 3000 cm⁻¹ versus time. Spectra were recorded until the water adsorption bands no longer changed with time. Total drying time was 2 hours. The same procedure described for the hydrated sample was followed and the sample was analyzed at CO₂ pressures of 0.5, 1.9, 3.2, 4.6, and 5.9 MPa.

3. RESULTS AND DISCUSSION

Infrared spectroscopy has been used extensively to characterize clay minerals and to examine the hydration state of smectites. The infrared spectrum of clay minerals were first characterized by Farmer (1974) who identified Mt H-O-H stretching vibrations at ~3630 cm⁻¹ produced by structural H₂O in the clay mineral. Bishop et al. (1994) further investigated the role of H₂O in Mt by identifying structurally bound H₂O as well as loosely-attached surface-bonded H₂O molecules that could be removed during dehydration. Later, Bishop et al. (2002) extended these initial studies by examining interactions between H₂O and different interlayer space cations in Mt. Bishop et al. (2002) found that as the Mts were dehydrated, a significant change in the OH band intensities near 3450 cm⁻¹ and 3350 cm⁻¹ was observed. This behavior indicates that the

addition or removal of nonstructural or interlayer space H₂O can be recognized based on the areas of peaks near 3450 cm⁻¹ and 3350 cm⁻¹. Recent work by Loring et al. (2014) quantitatively correlated Na⁺-Mt clay mineral expansion with adsorbed H₂O concentration in the presence of supercritical CO₂.

Two infrared spectroscopic experiments at 35°C were conducted on the Na⁺-STx-1 sample previously characterized by Rother et al. (2013) and these experiments are here identified as 1) hydrated and 2) relatively dehydrated experiments. The hydrated Na⁺-STx-1 is the as-received sample from Rother et al. (2013). Comparison of the FTIR data for the hydrated sample to results from Loring et al. (2014) indicates that the sample contains 8-12 mg H₂O per 1 gram of clay mineral, which corresponds to the transition from a single-layer to double-layer hydration state. The relatively dehydrated Na⁺-STx-1 is the as-received sample from Rother et al. (2013) that was dried as described above to remove interlayer water. Despite drying the Na⁺-STx-1 *in situ* at 98°C in the infrared cell for two hours, H₂O was still detected during FTIR analysis; this result is not surprising as previous studies have shown that complete dehydration requires heating to 200°C in a muffle furnace (Giesting et al., 2012). Comparison of the IR spectrum to those in Loring et al. (2014) indicates that each gram of clay mineral contained about 2 mg of H₂O, which translates to a hydration state of less than one water layer.

The interaction of CO₂ with Na⁺-STx-1 was investigated at pressures up to 5.9 MPa, a range that lies between CO₂ pressures of <120 torr (<0.016 MPa) and 9 MPa explored in previous FTIR studies on clay mineral-CO₂ interaction (Fripiat et al., 1974; Loring et al., 2012; Loring et al., 2014). Further, Giesting et al. (2012) reported that *d*₀₀₁ value remained unchanged for Na⁺-Mt (SWy-2) at pressures above 5 MPa PCO₂, despite working at pressures up to 64 MPa; hence, in this study pressures below 5.9 MPa were targeted.

3.1 Spectral Characterization of Na^+ Mt (Na^+ -STx-1)

Spectra of the hydrated and relatively dehydrated Na^+ -STx-1 are shown in Figure 3. Hydrated Na^+ -STx-1 absorption peaks include: (1) a peak at 791cm^{-1} corresponding to cristobalite, (2) a peak at 842cm^{-1} representing the in-plane librations of AlMgOH , (3) a peak at 914cm^{-1} corresponding to the in-plane librations of AlAlOH , (4) an Si-O stretching mode at 1030cm^{-1} , (5) an H-O-H bending mode at 1630cm^{-1} , (6) an H-O-H asymmetric and symmetric stretch near 3400cm^{-1} associated with nonstructural (interlayer space) water that is easily lost upon heating, (7) a band at 3620cm^{-1} corresponding to the hydroxyl group at the aluminum-enriched octahedral positions, and (8) a band at 3214cm^{-1} representing the H-O-H bending overtone mode (Figure 3, top spectrum). Gas phase asymmetric and symmetric stretching modes of water are at 3756 and 3657cm^{-1} , respectively. Typically when water condenses, these bands collapse into a broad band centered near 3400cm^{-1} (Goodman et al., 2001). All peaks were characterized according to data from Madejova and Komadel (2005). Residual cristobalite corresponding to the band at $\sim 791\text{cm}^{-1}$ was also detected by Madejova and Komadel (2005) and Rother et al. (2013). The peak at $\sim 3400\text{cm}^{-1}$ associated with nonstructural H_2O confirms that the as-received hydrated Na^+ -STx-1 sample from Rother et al. (2013) contains interlayer water.

Relatively dehydrated Na^+ -STx-1 absorption peaks (Figure 3, bottom spectrum) include the same spectral bands as the hydrated Na^+ -STx-1 sample with the following exceptions: (1) the peak at 842cm^{-1} representing AlMgOH in-plane librations is shifted to 849cm^{-1} . This spectral shift is consistent with data reported by Sposito et al. (1983) where a shift in the position of the AlMgOH peak is observed as the sample was dehydrated, reflecting a shift in the positions of the interlayer space cations as a result of dehydration. (2) The OH bending mode at 1630cm^{-1} and OH stretches near 3400cm^{-1} decreased in intensity indicating loss of nonstructural water. The

band at 3620 cm^{-1} corresponding to hydroxyl groups associated with aluminum-enriched octahedral positions shifted to 3624 cm^{-1} in response to the removal of interlayer water and shifting of positions of interlayer space cations.

3.2 Interaction of CO_2 with Na^+Mt ($\text{Na}^+\text{-STx-1}$)

In order to understand the binding sites of CO_2 and role of water molecules in the $\text{Na}^+\text{-STx-1}$ interlayer space, the adsorption/absorption behavior for CO_2 was investigated by using *in-situ* ATR-FTIR spectroscopy. Both hydrated and relatively dehydrated $\text{Na}^+\text{-STx-1}$ were examined because recent studies have shown that the presence of interlayer water is an important factor for CO_2 intercalation and that the expansion of the Mt structure when CO_2 is added is dependent on how much interlayer water is present at the beginning of the experiment (Giesting et al., 2012; Loring et al., 2014).

For hydrated $\text{Na}^+\text{-STx-1}$, the interaction of CO_2 with $\text{Na}^+\text{-STx-1}$ was monitored as a function of increasing pressure by using ATR-FTIR spectroscopy (Figure 4a, top spectra). Positive absorption bands at 2343 cm^{-1} and 660 cm^{-1} were observed and these grew in intensity as CO_2 pressure was increased from 0.5 to 5.8 MPa. These absorption bands are slightly red shifted from their gas-phase values of 2349 and 667 cm^{-1} , respectively. The absorption bands are consistent with the assignment of the ν_3 anti-symmetric stretching mode (2343 cm^{-1}) and ν_2 bending mode (660 cm^{-1}) associated with a physically adsorbed/absorbed CO_2 , i.e., a CO_2 molecule that is weakly interacting with a surface and rotationally constrained (see further discussion below). As discussed below, the slight red shift of the ν_3 mode and slight distortion of the ν_2 mode is consistent with weak electrostatic interactions of the CO_2 in the interlayer space. If the CO_2 was interacting with the Na^+ cations directly, one would expect a blue shift from the gas phase value of the ν_3 antisymmetric stretch near 2353 cm^{-1} (Llabres i Xamena,

2002; Gregoire et al., 2003; Ricks et al., 2013). This assignment is consistent with Loring et al. (2012) who reported the first direct evidence of CO₂ intercalation into a one water layer Ca⁺⁺Mt (Ca-STX-1) and identified linear CO₂ molecules that were rotationally constrained by more than one preferential interlayer space surface cation or water binding mode using ATR-FTIR. As such, the modes at 2343 cm⁻¹ and 660 cm⁻¹ represent CO₂ rotationally constrained in the Na⁺-STx-1 interlayer space.

A single ν_3 anti-symmetric stretching mode at 2343 cm⁻¹ is consistent with a single environment for CO₂ interaction in the Na⁺-STx-1 interlayer space. If alternative sites or mechanisms were available in the interlayer space or external surfaces, multiple anti-symmetric stretching modes would be observable for each CO₂ environment. If CO₂ interaction is occurring on the external surfaces of the Na⁺-STx-1, it is not observable with ATR-FTIR and/or the mechanism is not discernable between CO₂ intercalating in the interlayer space versus CO₂ interacting with the external surfaces. It should be noted that although the ν_3 stretching band at 2343 cm⁻¹ refers to CO₂ constrained in the Na⁺-STx-1 interlayer space, this spectral signature is not unique and is also recognized for CO₂ interacting in various host materials that do not have an interlayer space, such as polymers (2341-2335 cm⁻¹), zeolites (2368-2342 cm⁻¹), metal organic frameworks (2341-2332 cm⁻¹), carbon (2341-2328 cm⁻¹), and coal (2337-2332 cm⁻¹) (Kauffman et al., 2011).

The ν_2 CO₂ bending mode at 660 cm⁻¹ is rather broad and undefined (Figure 4a). The ν_2 bending mode is degenerate and can split into an in-plane bend at lower frequency and an out-of-plane bend at higher frequency upon a loss of linear symmetry. The degree of loss of degeneracy is related to the breadth of the ν_2 split and can reveal mechanistic information in regards to the CO₂ environment such as Lewis base, Lewis acid, and electrostatic interactions. A broad ν_2 peak

with little splitting suggests the CO₂ interaction in the interlayer space is weak, the molecule is rotationally constrained, and the linear symmetry is mostly retained. Together, the slight red shift of the ν_3 anti-symmetric stretching mode to 2343 cm⁻¹ and the broad undefined ν_2 bending mode at 660 cm⁻¹ suggest that electrostatic interactions are the dominant mechanism of the intercalated CO₂.

The interaction of CO₂ with relatively dehydrated Na⁺-STx-1 was also monitored as a function of increasing pressure by ATR-FTIR spectroscopy (Figure 4b, bottom spectra). Similar to the more hydrated clay mineral, positive absorption bands at 2343 cm⁻¹ and 660 cm⁻¹ were also observed. These absorption bands grew in intensity as CO₂ pressure was increased from 0.5 to 5.9 MPa and are assigned to the ν_3 anti-symmetric stretching mode (2343 cm⁻¹) and ν_2 bending mode (660 cm⁻¹) associated with CO₂ molecules rotationally constrained in the interlayer space of Na⁺-STx-1. At higher CO₂ pressure, the ν_3 anti-symmetric stretching mode shifts from 2343 to 2340 cm⁻¹, indicating stronger interaction with the Na⁺-STx-1 at higher pressure. The ν_2 bending mode at 660 cm⁻¹ is less noisy and better defined when compared to the hydrated sample. These absorption bands suggest that the CO₂ environment is similar in the hydrated and relatively dehydrated Na⁺-STx-1, but the interaction with the relatively dehydrated Na⁺-STx-1 may be somewhat stronger based on the better-defined, broad ν_2 bending mode and the fact the ν_3 anti-symmetric stretching mode shifts further towards the red with increasing CO₂ pressure.

In order to examine CO₂ intercalation of the hydrated and relatively dehydrated samples further, isotherms were constructed using the infrared data. A non-quantitative isotherm was created by integrating peak area of the ν_3 anti-symmetric stretching mode (2390-2310 cm⁻¹) of hydrated and relatively dehydrated Na⁺-STx-1 (Figure 4a,b) and plotting peak area versus CO₂ pressure (MPa) (Figure 5). It is interesting that more CO₂ appears to be intercalated in the

relatively dehydrated Na⁺-STx-1 compared to the more hydrated clay mineral and that the difference increases with increasing pressure until about 4.5 MPa, when the results start to converge slightly. This is consistent with the recorded difference in CO₂ interaction strength as a function of the hydration state of the clay mineral, as discussed above. Further, these results are consistent with Busch et al. (2008) who reported higher adsorption/absorption for clay minerals such as Mt, kaolinite, and illite dried at 105°C for 90 minutes when compared to as-received clay minerals. In order to further compare the isotherm shape with the excess adsorption measurements reported by Rother et al. (2013) on the same Na⁺-STx-1 material, CO₂ pressure was converted to bulk fluid densities using the Span and Wagner equation of state (Rother et al., 2013). The ATR-FTIR peak areas (2390-2310 cm⁻¹cm⁻¹) of hydrated and relatively dehydrated Na⁺-STx-1 (Figure 4a,b) were plotted as a function of CO₂ bulk density (g/cm³) and are shown in Figure 6 on the y₂ (right-side) axis. Plotted on the y₁ (left-side) axis for comparison are the gravimetric excess data in terms of interlayer space density of CO₂ (g/cm³) data by Rother et al. (2013). Both data sets show a linear trend for hydrated Na⁺-STx-1 at low CO₂ fluid densities.

The hydroxyl region between 4000 and 2900 cm⁻¹ was also monitored as a function of increasing CO₂ pressure for both hydrated and relatively dehydrated Na⁺-STx-1. Figure 7 shows the hydroxyl spectral region for hydrated and relatively dehydrated Na⁺-STx-1 at approximately 0, 0.5, 3.1, and 5.9 MPa CO₂ in both regular absorbance mode (CO₂ and Na⁺-STx-1 processed to a blank background) and difference mode (CO₂ and Na⁺-STx-1 processed to Na⁺-STx-1 prior to CO₂ introduction). The regular and difference spectra show no changes in spectral band positions or areas as CO₂ is introduced. This indicates that the interlayer water content remained constant during CO₂ exposure.

These results are consistent with both Rother et al. (2013) and Schaef et al. (2012) who reported that interlayer water was not displaced upon exposure of a one water layer Mt to CO₂ and the composition of the interlayer space did not change over the CO₂ pressure range studied. Rother et al. (2013) showed that upon exposure of a one water layer Na⁺-STx-1 to CO₂, the Bragg distance increased by 0.5 Å in the z direction. They suggested that CO₂ substitutes for the missing water molecules to stabilize the interlayer space region to a full one-layer hydration state. Giesting et al. (2012) showed that a Na⁺-Mt (SWy-1) in a dehydrated state with corresponding Bragg distance of 10.5 Å expanded to a full one-layer hydration state with a Bragg distance of 12.5 Å upon exposure to CO₂.

The infrared data reported here suggest that interlayer water is not displaced by CO₂ as the interlayer water content remains constant for both hydrated and relatively dehydrated Na⁺-STx-1 upon CO₂ exposure. When compared to the hydrated Na⁺-STx-1, the relatively dehydrated sample can accommodate relatively more CO₂ owing to less competition from nonstructural H₂O in the interlayer space. The results are consistent with Loring et al. (2014) who showed, albeit under supercritical CO₂ conditions, that the integrated absorbance of the CO₂ asymmetric stretching band increases as the adsorbed H₂O increases from zero (dehydrated) to a single water layer, but then decreases as the adsorbed H₂O concentration continues to increase. In other words, the presence of a small amount of H₂O helps to prop open the interlayer space, facilitating intercalation of CO₂, but too much H₂O inhibits intercalation of CO₂.

The absorption bands corresponding to the AlAlOH or AlMgOH vibrations at 914 and 842 cm⁻¹ were also monitored as a function of increasing CO₂ pressure for both hydrated and relatively dehydrated Na⁺-STx-1. The peak positions and areas remained unchanged within the analytical resolution of 2 cm⁻¹ at all pressures. This behavior is interpreted to indicate that as

CO₂ enters the interlayer spacing, CO₂ is not perturbing vibrations associated with the AlAlOH and AlMgOH sites.

Giesting et al. (2012) suggested the possible formation of carbonate in the interlayer spaces of Na⁺-Mt following exposure to CO₂. The FTIR spectra obtained in this study showed no evidence of bicarbonate, carbonate, or carbonic acid formation, which agrees with the findings from Loring et al. (2012). Chemical interaction between CO₂, nonstructural water, and Na⁺-Mt would be discerned by new absorption bands near 1700, 1400, 831, and 720 cm⁻¹ for carbonate-like species. Because these absorption bands were not observed, it was interpreted that chemical interactions between CO₂ and Na⁺-STx-1 did not occur.

3.3 Interaction of N₂ with Na⁺ Mt

The hydrated and relatively dehydrated Na⁺-STx-1 were characterized under pressure in a N₂ environment up to 8.8 MPa. When compared to the spectrum of the Na⁺-STx-1 before exposure to any gas (i.e., at ambient pressure), all of the characteristic Na⁺-STx-1 peaks were present and unchanged during exposure to N₂, indicating that N₂ does not interact with the Na⁺-STx-1 structure and that pressure alone does not affect peak position or area over the range of pressures of this study. These results are consistent with Schaef et al. (2012) who did not observe expansion of a one water layer Ca⁺⁺Mt upon exposure to dry N₂. These results, in turn, support our interpretations that the changes in FTIR spectra that are observed upon exposure to CO₂ are the result of CO₂ interaction with Na⁺-STx-1.

3.4 Temperature Effects

To test the effect of temperature on CO₂ – Na⁺-STx-1 interactions, the same hydrated Na⁺-STx-1 sample that was previously run at 35°C was run at 50°C and at 0.3 MPa. No

significant differences in peak positions (within the analytical resolution of $\pm 2 \text{ cm}^{-1}$) or peak areas for the AlAlOH, AlMgOH, and CO₂ bands were observed. Rother et al. (2013) concluded that interlayer spacing is not affected by changes in temperature, but CO₂ density in the interlayer space does increase slightly at higher temperature and pressure.

4. CONCLUSIONS

The results of this work show that CO₂ is rotationally constrained in the interlayer space of both hydrated (containing layers with both one- and two-water layers) and relatively dehydrated (containing both dehydrated layers and one-water layers) Na⁺-STx-1. Together, the red shift of the ν_3 anti-symmetric stretching mode to 2343 cm^{-1} and the broad undefined ν_2 bending mode at 660 cm^{-1} suggest that CO₂ interaction in the interlayer space is weak, the molecule is rotationally constrained, and the linear symmetry is mostly retained; this former observation is consistent with those of Fripiat et al. (1974) made at much lower temperatures and pressures, and with Loring et al. (2012) and Loring et al. (2014) under supercritical CO₂ conditions. Interlayer water is not displaced by CO₂ as the interlayer water content remains constant for both hydrated and relatively dehydrated Na⁺-STx-1 upon CO₂ exposure. When compared to the hydrated Na⁺-STx-1, the relatively dehydrated sample can accommodate more CO₂ due to less competition from nonstructural H₂O in the interlayer space. No spectral evidence of bicarbonate, carbonate, or carbonic acid formation was observed, suggesting that no chemical interactions occurred between Na⁺-STx-1, nonstructural water, and CO₂. Future spectroscopic and XRD measurements are recommended to further discern the interaction of CO₂ and Mt under a broader range of hydration conditions and CO₂ pressure environments. By

improving the understanding of how CO₂ interacts with Mt at CCUS temperature and pressure conditions, the most appropriate geologic environments for sequestration can be targeted and the long-term behavior of the formation can be predicted with a higher degree of confidence.

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Figures

Figure 1: Schematic representation depicting the injection of CO₂ from a fossil fuel power plant into a saline formation beneath a shale cap rock. The CO₂ is buoyant relative to the saline brine in the pores and rises to the top of the formation where it may interact with the clay-rich shale cap rock. The relative abundance of CO₂ in the formation as a function of distance from the wellbore is represented by the color gradient from red (more CO₂) to pink (less CO₂).

Figure 2: Schematic representation of the Mt /water /CO₂ system. Color designation: red balls – oxygens; purple – sodium ions; white – hydrogens; gray – carbon (Myshakin et al., 2013).

Figure 3: FTIR spectrum of hydrated and relatively dehydrated Na^+ -STx-1. The labeled peaks correspond to: (1) a peak at 791 cm^{-1} corresponding to cristobalite, (2) a peak at $849\text{--}842\text{ cm}^{-1}$ representing the in-plane librations of AlMgOH , (3) a peak at 914 cm^{-1} corresponding to the in-plane librations of AlAlOH , (4) an Si stretching mode at 1030 cm^{-1} , (5) an H-O-H bending mode at 1630 cm^{-1} , (6) an H-O-H asymmetric and symmetric stretch near 3400 cm^{-1} associated with nonstructural (interlayer space) water readily lost upon heating, (7) a band at $3624\text{--}3620\text{ cm}^{-1}$ corresponding to the hydroxyl group at the aluminum-enriched octahedral positions, and (8) a band at 3214 representing the H-O-H $2\nu_2$ bending overtone mode.

Figure 4: a) ν_3 CO_2 asymmetric stretch (2343 cm^{-1}) and ν_2 CO_2 bending mode (660 cm^{-1}) of CO_2 constrained in the hydrated Na^+ -STx-1interlayer space as a function of increasing CO_2 pressure - 0.5, 1.8, 3.1, 4.5, 5.8 MPa. b) ν_3 CO_2 asymmetric stretch (2343 cm^{-1}) and ν_2 CO_2 bending mode (660 cm^{-1}) of CO_2 constrained in the relatively dehydrated Na^+ -STx-1interlayer space. 0.5, 1.9, 3.2, 4.6, 5.9 MPa

Figure 5: Integrated area of the ν_3 CO₂ asymmetric stretch (2343 cm⁻¹) versus CO₂ pressure (MPa) for hydrated and relatively dehydrated Na⁺-STx-1.

Figure 6: y₁ axis – Interlayer space Density of CO₂ (grams of CO₂ adsorbed/absorbed per cm³ of mineral) of supercritical CO₂ adsorbed/absorbed onto Na⁺-STx-1 versus CO₂ bulk density (g/cm³) as reported by Rother et al. (2013) y₂ axis - Integrated area of the ν₃ CO₂ asymmetric stretch (2343 cm⁻¹) shown in Figure 5 versus CO₂ bulk density (g/cm³).

Figure 7: a) The hydroxyl region between 4000 and 2900 cm⁻¹ for hydrated Na⁺-STx-1 as a function of CO₂ pressure (0, 0.5, 3.1, and 5.9 MPa CO₂) in both regular absorbance mode (CO₂ and Na⁺-STx-1 processed to a blank background) and difference mode (CO₂ and Na⁺-STx-1 processed to Na⁺-STx-1 prior to CO₂ introduction). b) The hydroxyl region between 4000 and 2900 cm⁻¹ for relatively dehydrated Na⁺-STx-1 as a function of CO₂ pressure (0, 0.5, 3.1, and 5.9 MPa CO₂) in both regular absorbance mode (CO₂ and Na⁺-STx-1 processed to a blank background) and difference mode (CO₂ and Na⁺-STx-1 processed to Na⁺-STx-1 prior to CO₂ introduction)

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