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Abstract

To clarify the mechanisms of carbonation of clay minerals, such as bentonite, kaolinite, and soft clay, we exposed them to supercritical carbon dioxide ($scCO_2$)/water at temperatures of 200° and 250°C and pressures of 1500 and 2000 psi for 72- and 107-hours. Bentonite, comprising three crystalline phases, montomorillonite (MMT), anorthoclase-type albite, and quartz was susceptible to reactions with ionic carbonic acid yielded by the interactions between $scCO_2$ and water, particularly MMT and anorthoclase-type albite phases. For MMT, the cation-exchangeable ions, such as Na^+ and Ca^{2+}, present in its basal interplanar space, were replaced by proton, H^+, from ionic carbonic acid; thereafter, the cations leaching from MMT directly reacted with CO_3^{2-} as a counter ion of H^+ to form carbonate compounds. Such *in-situ* carbonation process in basal space caused the shrinkage and breakage of the spacing structure within MMT. In contrast, the wet carbonation of anorthoclase-type albite, categorized as rock minerals, entailed the formation of three amorphous by-products, such as carbonates, kaolinite-like compounds, and silicon dioxide. Together, these two different carbonations caused the disintegration and corruption of bentonite. Kaolinite clay containing the amorphous carbonates and silicon dioxide was inert to wet carbonation. We noted only a gain in weight due to its water uptake, suggesting that kaolinite-like by-products generated by the wet carbonation of rock minerals might remain unchanged even during extended exposure. Soft clay consisting of two crystalline phases, dolomite and silicon dioxide, also was unaltered by wet carbonation, despite the uptake of water.

Introduction

Assuming that supercritical carbon dioxide ($scCO_2$) is applied as an alternative working fluid to Enhanced Geothermal System (EGS), our previous study [1] focused on gaining a fundamental understanding of the effect of wet carbonation mechanisms on several pure rock minerals present in an impermeable hot rock stratum, after exposure to $scCO_2$/water at 250°C and 2500 psi pressure. Our results revealed that all rock minerals including granite, albite, hornblende, and diorite, were susceptible to reactions with $scCO_2$/water under such a harsh environment. Their reactions led to the formation of three amorphous reaction products, such as carbonates, aluminum silicate hydroxide-based clay-like compounds, and silicon dioxide. Hence, a considerable attention was paid to the solubility of carbonate compounds containing Na, K, Ca, Mg, and Fe in a hot water, in particular, for alkali metal carbonates, Na_2CO_3 and K_2CO_3. The solubility of these carbonates was more than 3 x 10^2 times higher than that of other carbonates [2], raising concerns that their dissolution might cause the development of porous micro-or nano-structure in the reservoir rock foundation. After exposing the anorthoclase-type albite [$(Na,K)AlSi_3O_8$] phase in the granite and the albite ($NaAlSi_3O_8$) phase-based rock to hot $scCO_2$/water, these phases formed the Na- or K-carbonates, while the carbonated hornblende and diorite rocks yielded Ca-, Mg-, and Fe-carbonates, which were categorized as product of lower water solubility.

The other attention was the physicochemical behaviors of aluminum silicate hydroxide-based clay-like by-products because some clay minerals display undesirable properties, such as a large water uptake, disintegration, and excessive volume expansion that might generate *in-situ* stress in critical boundary zones between clay and non-clay mineral layers. The chemistry of clay-like by-products derived from these rock minerals was similar to that of kaolinite clay, $Al_2Si_2O_5(OH)_4$.

Based upon this information, our emphasis in this present study was directed towards exploring the wet carbonation of several pure clay minerals, such as bentonite, kaolinite, and soft clay. Although only little amounts, if any, of these clay minerals are present in the EGS reservoir rock foundation, some might coexist with the major rock mineral layer. The parameters to be studied included changes in the weight of bulk clay minerals after exposure to $scCO_2$/water at 250°C, the mechanism of carbonation, and the identification of carbonation reaction by-products. The integration of all data obtained provides us with pivotal information on the susceptibility of these

clays to hot wet carbonation, and on whether the kaolinite-like clay by-products yielded therein remain unaltered after an extended exposure period.

Experimental

Three clay minerals, bentonite, kaolinite, and soft clay, were obtained from Rockman's Trading Post, Inc. Two different exposure tests were set in this study: One was the exposure of bulk clay mineral samples to $scCO_2$/water at the temperature of 250°C and the pressure of 2000 psi for 104 hours; the other was to expose the powdered wet clay samples in a $scCO_2$ containing autoclave at 200°C and 1500 psi pressure for 72 hours. The procedure adapted in the first test was as follows; 1) all bulk minerals were placed in an autoclave containing water, 2) autoclave's temperature was raised to 120°C to create steam, 3) $scCO_2$ was injected into steamy autoclave under the pressure of 2000 psi, and 4) autoclave's temperature was raised to 250°C. For the second test, the powdered samples were prepared in the following sequence; all clay minerals were broken and ground to make the powders with a particle size of < 0.2 mm, and then the powders were mixed with water to prepare mineral pasts. The water/powdered clay ratios by weight were 0.64, 1.45, and 0.41 % for kaolinite, bentonite, and soft clay, respectively. Then, the pasts were packed into 1 cm in diameter and 5 cm long quartz vials; the thickness of the paste adhering to vial wall's surface was approximately 3 mm. The vials then were exposed in a $scCO_2$ saturated autoclave.

Thereafter, all bulk and powder samples were dried in an oven at 100°C for 24 hours to eliminate all free moisture adsorbed in the samples. For the bulk samples, we observed the alterations in their appearance, and also determined the changes in weight. For the powdered samples, two analytical tools, x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR), were employed to identify amorphous and crystalline carbonation products, and to estimate the extent of the susceptibility of these minerals to reaction with $scCO_2$.

Results and Discussion

Changes in Appearance and Weight

Table 1 and Figure 1 show that bentonite severely suffered from wet carbonation, causing its disintegration during exposure. In contrast, two clays, kaolinite (Figure 2) and soft clay (not shown), remained intact, though their colors were changed from white to brown; further, their weight increased by 4.26 % and 7.98 %, respectively, after exposure. However, this limited information did not allow us to judge whether their weight gain and change in color was due to their wet carbonation or due to moisture uptake, and/or both.

In response to this question, we undertook XRD and FT-IR analyses for the unexposed and exposed clay powders.

XRD and FT-IR Analyses

Bentonite

Figure 3 compares the XRD patterns of bentonite clay before and after exposure for 3 days to wet/scCO_2 at 200°C and 1300 psi pressure. As is evident, unexposed bentonite consisted of three crystalline phases, montomorillonite [MMT, hydrated sodium calcium aluminum magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O$], anorthoclase-type albite [$(Na,K)AlSi_3O_8$], and quartz (SiO_2). Regarding the MMT, categorized as layered silicate clay mineral, it was constituted by one alumina octahedral sheet sandwiched between two silica tetrahedral sheets. The basal interplanar space of ~ 1.2 nm between the alumina and silica sheets encompasses reactive Na^+ and Ca^{2+} ions. In contrast, anorthoclase-type albite can be categorized as non-layer silicate rock mineral.

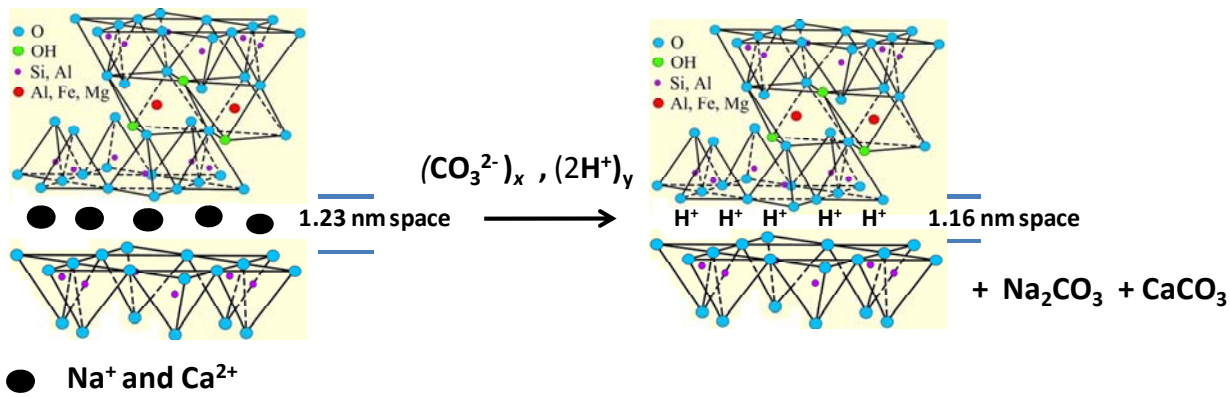
After exposure, the XRD pattern of exposed samples quite differed from that of unexposed control. There were two major differences: One was a striking decay of MMT-related line intensity at 1.227 nm d_{001}-spacing, while this spacing was shifted to lower site at 1.162 nm; the other was a conspicuous reduction of anorthoclase-type albite's line intensity at 0.315 nm d_{002}-spacing. Since the *d*-spacing at 1.227 nm in MMT represents its basal space, such a decay of line intensity at 1.227 nm and a shift downwards of its line position can be explained by the disintegration and shrinkage of this opening basal space. As well documented by many investigators [3-7], these reactive cations present in this open space have the cation-

exchangeable behaviors. Thus, it is reasonable to rationalize that these cations might be exchanged by proton, H^+, from the ionic carbonic acid, ($H_2CO_3 \leftrightarrow 2H^+ + CO_3^{2-}$), yielded by the reactions between CO_2 and H_2O. This exchange of H^+ with the Na^+ and Ca^{2+} ions caused the breakdown and shrinkage of opening basal space. The XRD pattern also demonstrated that the line intensity of the other MMT-related *d*-spacings remained unchanged. Thus, the layered silicate sheets within MMT were unaffected by wet carbonation under these test conditions. Regarding the reduction of intensity of anorthoclase-type albite's line, our previous study on carbonation of rock minerals by $scCO_2$ [1] revealed that anothoclase-type albite was susceptible to reactions with $scCO_2$ in aqueous media at 250°C and 2500 psi pressure. We proposed the following carbonation mechanism; $2(Na,K)AlSi_3O_8 + 2CO_3^- + 4H^+ \rightarrow Na_2CO_3 + K_2CO_3 + Al_2Si_{6-x}O_{12-2x}(OH)_4 + xSiO_2$. As a result, four wet carbonation reaction by-products, such as the Na and K carbonates, clay-like mineral [$Al_2Si_{6-x}O_{12-2x}(OH)_4$, containing SiOH groups], and silicon dioxide, were formed as amorphous phases.

Figure 4 illustrates the FT-IR spectra of bentonite before and after exposure to $scCO_2$/water. The spectrum of unexposed sample included the eight absorption bands. The first two bands at 1998 and 1865 cm^{-1} are attributed to the Si-O stretching vibration in crystalline quartz or amorphous silicon dioxide, SiO_2, while the band at 1636 cm^{-1} is related to the water absorbed in clay. At 1119 and 1048 cm^{-1}, these bands are associated with the oxygen-bridging Si-O-Si asymmetric stretching mode and non oxygen-bridging $Si\text{-}O^-$ stretching in the $Si\text{-}O^-\ Na^+$ or Ca^{2+} group, respectively, in the MMT and anothoclase-type albite. The O-H bending in the SiOH group, which represents a typical clay phase like MMT, is apparent at 917 cm^{-1}. The last two bands at 798 and 778 cm^{-1} belong to Al-O stretching in the MMT and anothoclase-type albite.

The exposed bentonite exhibited three different spectral features: First was the growth of quartz-related Si-O stretching bands at 1998 and 1865 cm^{-1}; second was the appearance of three new bands at 1467, 1400, and 976 cm^{-1}, and finally, the shoulder band of oxygen-bridging Si-O-Si before exposure became the major band. The first suggests that wet carbonation of bentonite generates additional quartz or amorphous silicon dioxide as carbonation reaction by-products. The contributor of two new bands at 1467 and 1400 cm^{-1} are carbonates, while the other new band at 976 cm^{-1} is likely to be associated with a newly formed SiOH group [8]. This data strongly supported information obtained from XRD study. Thus, when bentonite was exposed to

$scCO_2$/water at 200°C, two quite different carbonation reactions occurred: One was the carbonation of Na^+ and Ca^{2+} ions dissociated from MMT's basal space by the cation-exchanging reactions between the H^+ from the ionic carbonic acid and these cations in the MMT, thereby forming Na_2CO_3 and $CaCO_3$. We illustrate this dissociation → carbonation route below.



The other expressed the carbonation of anothoclase-type albite as shown earlier, signifying the formation of carbonates, such as Na_2CO_3 and K_2CO_3, coexisting with clay-like amorphous mineral, $Al_2Si_{6-x}O_{12-2x}(OH)_4$, and quartz, x$SiO_2$, as carbonation reaction by-products.

Thus, the wet carbonation of two different crystalline phases present in bentonite was detrimental to its integrity, causing its disintegration and decomposition.

Kaolinite

Figure 5 shows XRD tracing of kaolinite crystal, $Al_2Si_2O_5(OH)_4$, before and after exposure to $scCO_2$/water. The exposed sample displayed a very similar XRD pattern to the non-exposed one; thus, there were no pronounced changes in line intensity of all *d*-spacings and no appearance of new lines, compared with that of unexposed one, strongly demonstrating that kaolinite was unsusceptible to wet carbonation under this exposure condition.

Figure 6 compares the FT-IR spectral features of unexposed and exposed kaolinite. The spectrum of the former revealed that kaolinite clay contains amorphous chemical compounds. The bands at 1942 and 1825 cm^{-1} clearly represented the presence of amorphous silicon dioxide. In addition,

the presence of carbonated compounds is evidenced by the bands at 1457 and 1402 cm^{-1}. All bands in the range from 1200 to 700 cm^{-1} belong to the Kaolinite. Compared with this, the same feature of spectrum was recorded from the exposed specimen, strongly supporting the results from XRD study. Thus, the kaolinite containing silicon dioxide and carbonates as amorphous phases essentially does not react with ionic carbonic acid. Its increase in weight after exposure was primarily due to the uptake and retention of moisture, but not due to wet carbonation.

Relating this information to the kaolinite-like amorphous clay yielded as carbonation by-products of the single albite rock and the anothoclase-type albite phase present in the bentonite clay and granite rock, we concluded that the chemical affinity of such kaolinite-like by-products with ionic carbonic acid was minimal, if any. Therefore, this clay-like by-product might well remain unchanged though an extended exposure time.

Soft Clay

Figure 7 gives the XRD patterns of soft clay before and after $scCO_2$ exposure. The soft clay was composed of two crystalline phases, dolomite, $CaMg(CO_3)_2$, and quartz. Comparing the XRD pattern's features, there was no significant difference between samples before and after exposure, manifesting that these crystalline phases do not react with ionic carbonic acid. FT-IR test results (Figure 8) directly supported this information. In fact, the spectral feature of the exposed sample closely resembled that before exposure. Thus, soft clay had no chemical affinity with wet carbonation; its weight gain after exposure simply was due to uptake of water.

Conclusion

We reached the following conclusions from our studies on the exposure of three clay minerals, bentonite, kaolinite, and soft clay, to supercritical carbon dioxide ($scCO_2$)/water under two different conditions: One involved exposing bulk clay minerals for 107 hours at 250°C and 2000 psi pressure; the other was the exposure of powdered clay minerals for 72 hours at 200°C and 1500 psi pressure.

1. Bentonite consisted of three different crystalline phases, montomorillonite (MMT), anorthoclase-type albite, and quartz. The first two phases were susceptible to reactions with ionic carbonic acid yielded by interactions between $scCO_2$ and water. For MMT, the first step of its carbonation pathway was the exchange of Na^+ and Ca^{2+} present as cation-exchangeable elements in its ~ 1.2 nm basal interplanar space with hydrogen, H^+, in the carbonic acid; thereafter, these cations released from MMT directly reacted with CO_3^{2-} as the counter ion of H^+ to form carbonates. Such carbonation caused the shrinkage and disintegration of basal spacing. The wet carbonation of anorthoclase-type albite generated four wet carbonation derived amorphous by-products, Na- and K-carbonates, kaolinite-like clay compound, and silicon dioxide. These carbonations were degraded and disrupted the integrity of bentonite structure.

2. Kaolinite clay contained two amorphous phases, carbonates and silicon dioxide. Kaolinite crystal and these amorphous phases had no chemical affinity with ionic carbonic acid, reflecting the inertness of this clay to wet carbonation under this exposure condition. In fact, the exposed kaolinite remained intact even though it gained some weight by uptake of water. Seemingly, kaolinite-like by-products yielded from the wet carbonation of the rock minerals might sustain their integrity even after an extended exposure time.

3. Soft clay was composed of dolomite as the major crystal phase and quartz as the minor crystal phase, and it was unsusceptible to wet carbonation despite gaining weight by absorbing water.

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Table 1. Changes in weight and appearance of bulk clay minerals after exposure to $scCO_2$/water at 250°C for 107 hours.

Clay Mineral	**Changes in weight, %**	**Alternation of appearance**
Bentonite	-	Disintegration
Kaolinite	+ 4.26	Change in color from white to brown, no disintegration
Soft Clay	+ 7.98	Change in color from white to brown, no disintegration

Figure 1. Bentonite clay before (left) and after (right) exposure to $scCO_2$/water at 250°C.

Figure 2. Kaolinite before (left) and after (right) exposure to $scCO_2$/water at 250°C.

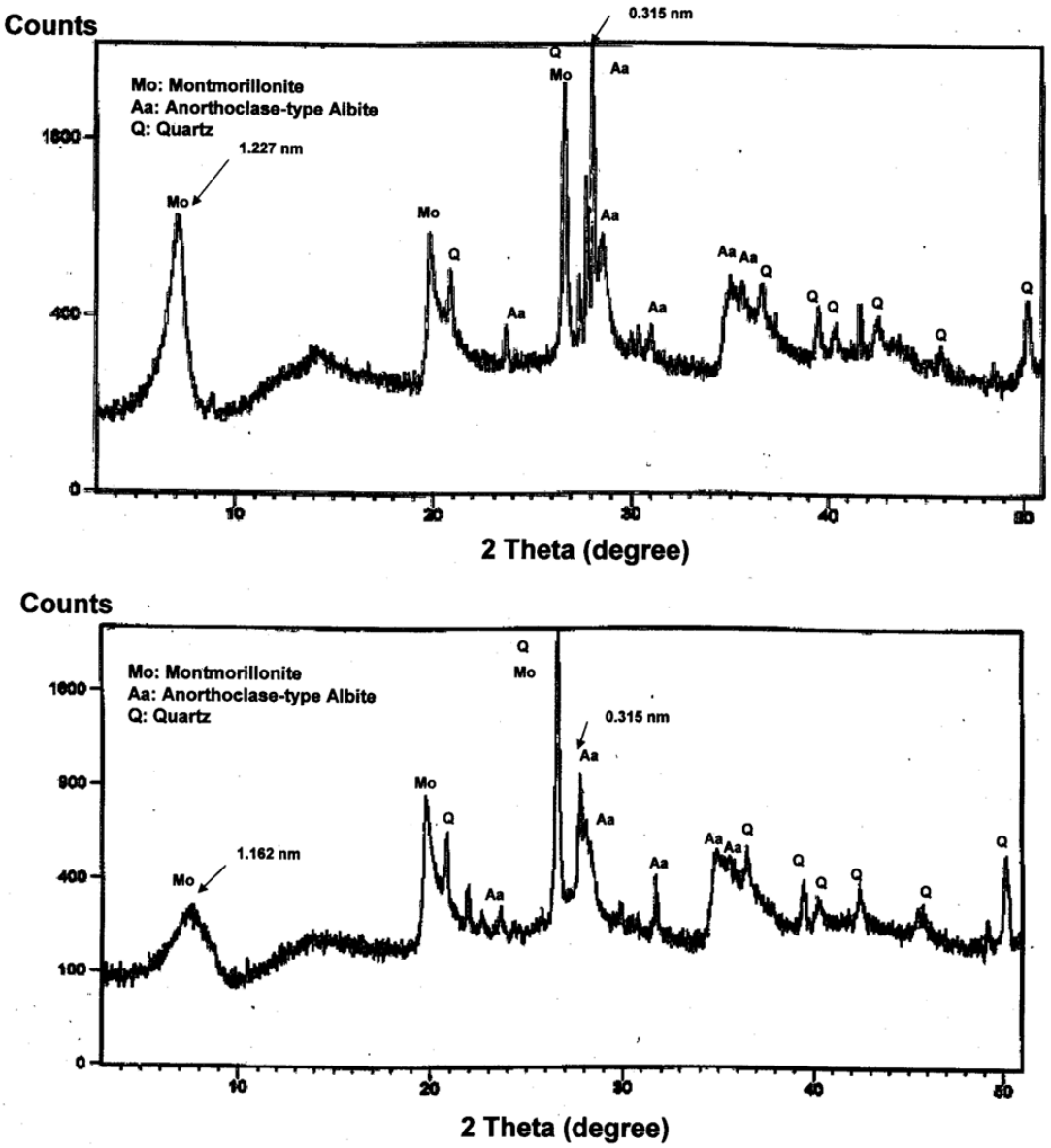

Figure 3. Comparison between XRD patterns of bentonite before (top) and after (bottom) exposure to $scCO_2$/water at 200°C.

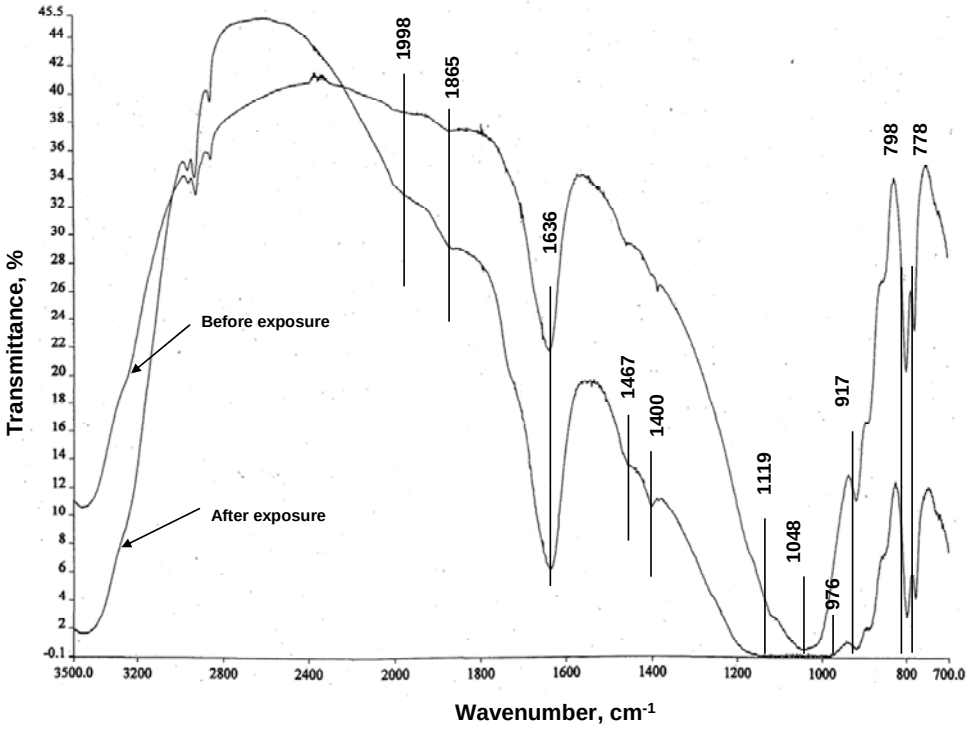

Figure 4. FT-IR spectra for exposed and unexposed bentonite.

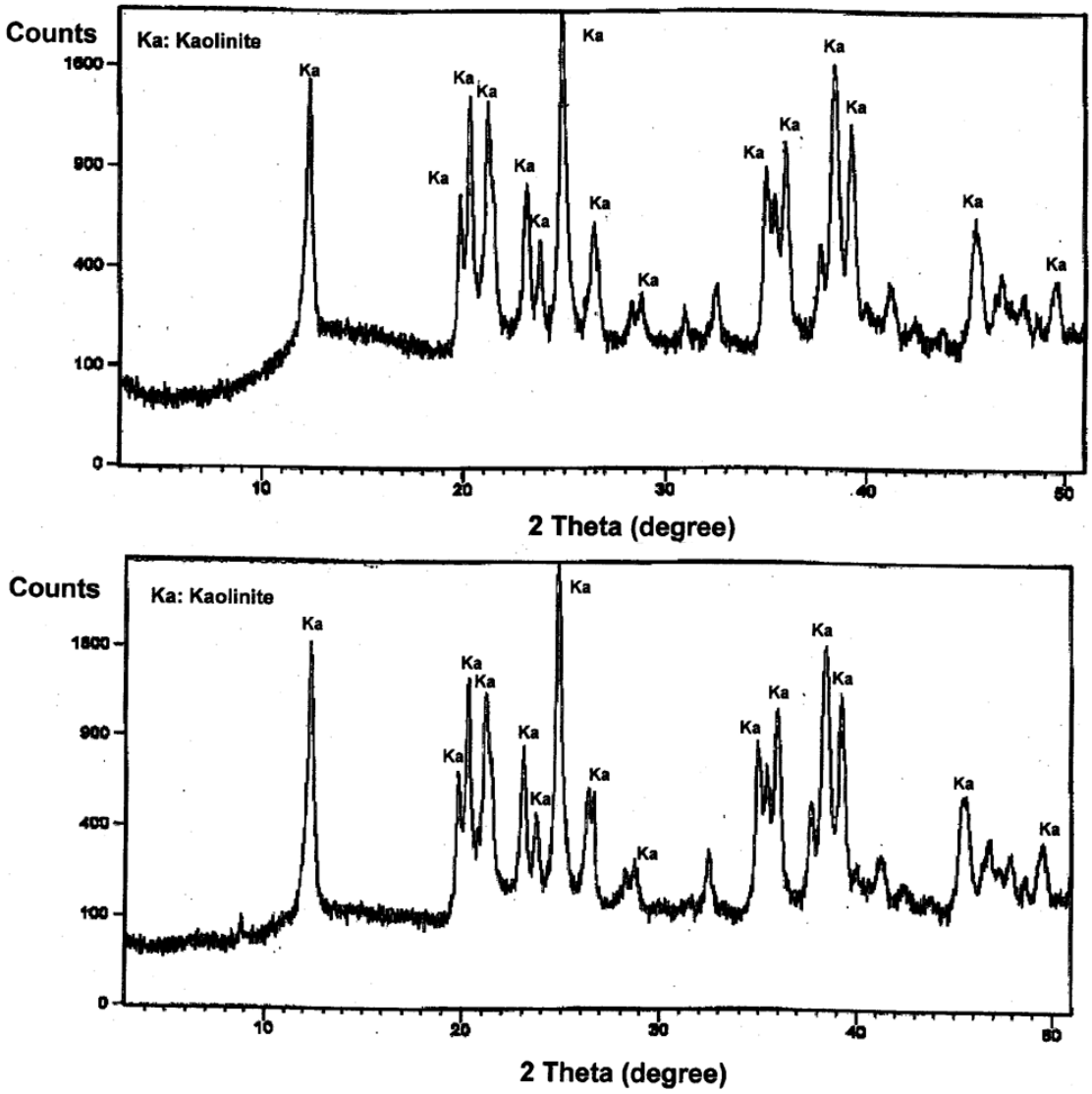

Figure 5. XRD tracing for kaolinite before (top) and after (bottom) exposure.

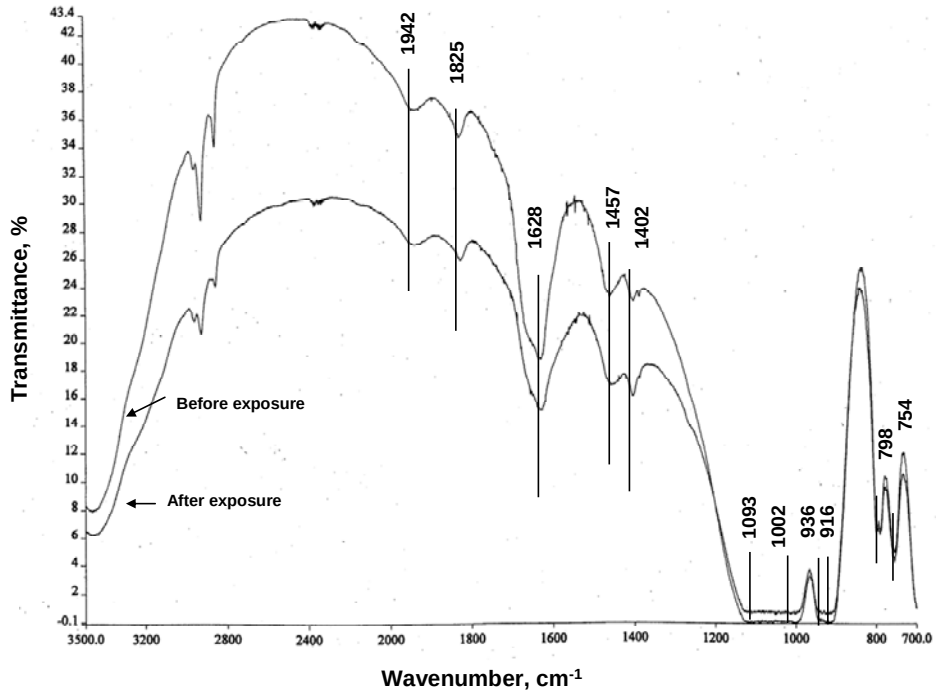

Figure 6. FT-IR spectra for unexposed and exposed kaolinite.

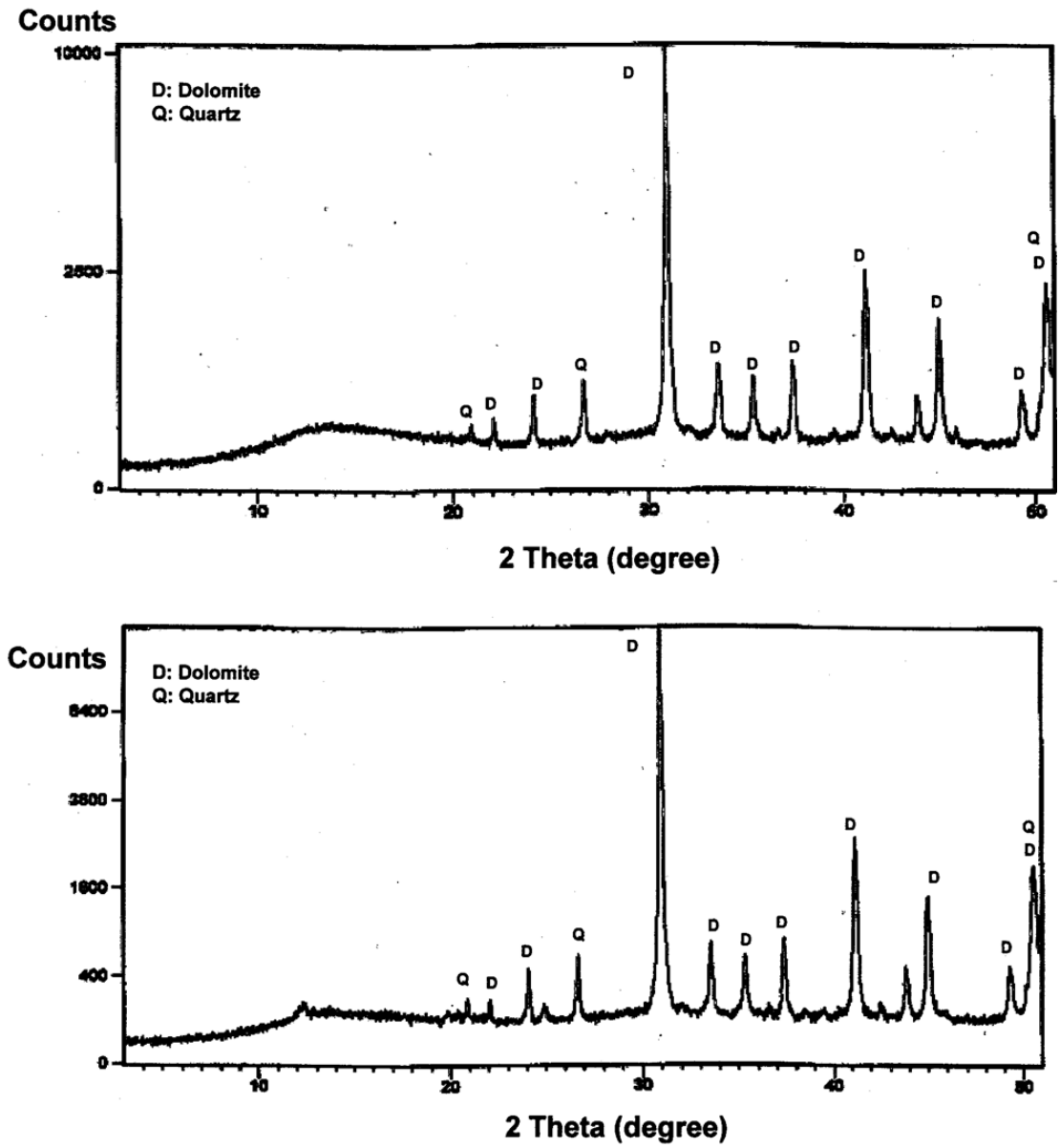

Figure 7. XRD data for exposed and unexposed soft clay.

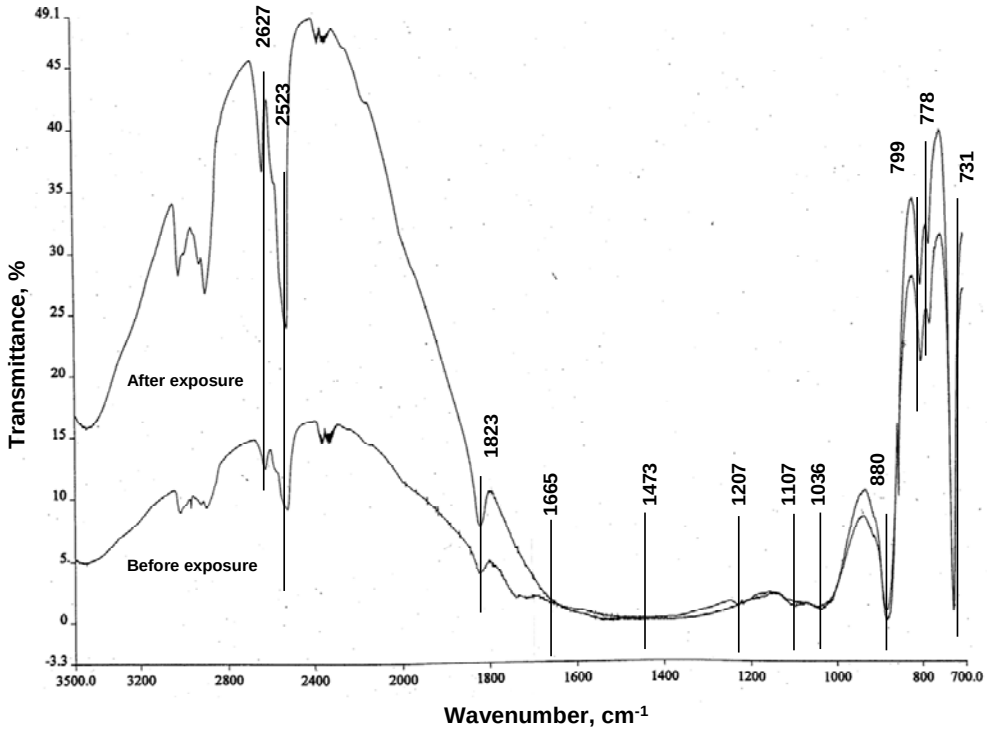

Figure 8. FT-IR results from exposed and unexposed soft clay.