JOURNAL of the MEXICAN CHEMICAL SOCIETY

https://www.jmcs.org.mx/

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J. Mex. Chem. Soc. **2026**, *70(1):e2520*

Received July 9th, 2025
Accepted November 11th

http://dx.doi.org/10.29356/jmcs.v70i1.2520
e-location ID: 2520

Keywords:
Firing; montmorillonite; structural iron; Mössbauer; isomer shift; quadrupole splitting

Palabras clave:
Calcinación; montmorillonita; hierro estructural; espectroscopía Mössbauer; desplazamiento isomérico; desdoblamiento cuadrupolar

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ISSN-e 2594-0317

Effects of Firing on Iron content of Wyoming Montmorillonite: Mössbauer and Photoacoustic Study

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Abstract. Montmorillonite MMT is a naturally occurring aluminosilicate layered mineral that is made of AlO_6 (octahedron) and SiO_4 (tetrahedron), sharing top oxygen atoms. The iron oxidation state in the crystal lattice of MMT clay is critical in determining the surface and colloidal chemistry. The changes in the behavior of the structural iron in Wyoming MMT clay, upon firing from 100 ºC up to 1000 ºC were investigated. The transformation of iron was monitored using Mössbauer spectroscopy as the main tool, and other changes were studied using photoacoustic spectroscopy. The clay samples were fired from 100 up to 1000 ºC. No formal change in the Mössbauer parameters was observed on firing the sample from 100 to 500 ºC except the oxidation of Fe(II) at about 200 ºC. The main changes in the Fe(III) Mössbauer parameters occurred upon firing from 600 ºC up to 1000 ºC. The isomer shift decreases gradually with increasing temperature of firing, due to the de-hydroxylation of the structure. The quadrupole splitting of the Fe(III) doublet increased, from 600 ºC to 1000 ºC, indicating an increase in distortion of the lattice as the temperature was raised. A slight increase in the linewidth of Fe(III) values of the fired samples from that of the original sample was also observed, suggesting that more than one iron site occurs. The photoacoustic investigations were in good agreement with Mössbauer results.

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ISSN-e 2594-0317

Resumen. La montmorillonita MMT es un mineral aluminosilicato laminar de origen natural, constituido por unidades de AlO_6 (octaedros) y SiO_4 (tetraedros), que comparten los átomos de oxígeno de sus vértices. El estado de oxidación del hierro en la red cristalina de la arcilla MMT es un factor crítico para determinar su química superficial y coloidal. Se investigaron los cambios en el comportamiento del hierro estructural presente en la montmorillonita de Wyoming al someterla a calcinación entre 100 °C y 1000 °C. La transformación del hierro se monitoreó principalmente mediante espectroscopía Mössbauer, mientras que otros cambios se estudiaron utilizando espectroscopía fotoacústica. Las muestras de arcilla fueron calcinadas a temperaturas comprendidas entre 100 y 1000 °C. No se observaron cambios significativos en los parámetros Mössbauer al calcinar las muestras entre 100 y 500 °C, con excepción de la oxidación del Fe(II), que ocurrió alrededor de 200 °C. Los principales cambios en los parámetros Mössbauer correspondientes al Fe(III) se produjeron al incrementar la temperatura de calcinación de 600 a 1000 °C. El desplazamiento isomérico disminuyó gradualmente con el aumento de la temperatura de calcinación, como consecuencia de la deshidroxilación de la estructura. El desdoblamiento cuadrupolar del doblete de Fe(III) aumentó entre 600 y 1000 °C, indicando un incremento en la distorsión de la red cristalina a medida que se elevaba la temperatura. Asimismo, se observó un ligero aumento en el ancho de línea de las señales de Fe(III) de las muestras calcinadas con respecto a la muestra original, lo que sugiere la existencia de más de un sitio cristalográfico para el hierro. Los estudios fotoacústicos mostraron una excelente concordancia con los resultados obtenidos mediante espectroscopía Mössbauer.

Introduction

There have been many reports on the firing of clay minerals [1-5]. Most of these studies focused on the physical, chemical, mineralogical and thermal properties of the clay and its ability to convert to ceramic materials [6-8]. Mineralogical and chemical characterization on fired clay from the Lake Van in Turkey were studied by X-ray diffraction. Two types of pastes for pottery production were identified [9]. Seven clay samples from northeast Algeria were also studied using X-ray diffraction, Fourier-transform IR spectra, X-ray fluorescence, scanning electron microscopy. The samples were fired at 800-1100 °C. The main transformations were shown to occur at 1000 °C by the appearance of new crystalline phases [10]. The mineralogical, physico-chemical and thermal analysis of Triassic clay from the southeastern Tunisia has demonstrated that a series of phase transformations may occur if the clay is fired up to 1150 oC [11]. Another study on fired clay from northwest Tunisia reported evidence for the main transformation occurring at 1000 °C (by the appearance of new crystalline phases) [12]. To determine their potential suitability as raw materials for varied ceramic applications, five different Moroccan clay samples were studied, and their physical, chemical, mineralogical and thermal characteristics were reported. The results revealed that two of the samples had adequate characteristics to produce structural ceramics [13]. The effects of thermal treatment, both on the rate of heating and the firing temperature of clay, have been studied to optimize the fabrication process and to obtain better mechanical properties. The results showed that rapid heating rates in the early stage of firing have great influence on the resulting mechanical properties [14]. Two Brazilian clay samples were fired at 850 to 1200 °C and studied for use in the production of red ceramics. Both the samples were shown to be highly plastic due to the presence of increased percentages of kaolinitic clay minerals [15]. To determine their suitability as raw materials in various ceramic applications, natural clay deposits from central Cambodia have been investigated for their physical, chemical, mineralogical, thermal and firing characteristics. A significant development of densification behavior of the resulting ceramics was found at temperatures above 1000 °C [16]. Five clay samples from three locations in the Denizli area (western Anatolia) were fired at 700-1200 °C and studied for their thermal behavior. Important densification at temperatures over 1000 °C was shown [17].

Mössbauer spectroscopy has proved to be an important probe for mineralogical and geochemical transformation. The technique has been extensively employed to probe electronic environments of iron that exist widely in clay minerals [18,19]. It also provides information on Fe2+ oxidation and shows subtle variations in the coordination and mineralogy of Fe site, including the formation iron oxides [20,21]. The

http://dx.doi.org/10.29356/jmcs.v70i1.2520

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aim of the investigation reported herein was to characterize a MMT clay by observing the changes that occur on structural iron metal during firing. This established the conditions and temperature ranges the clay could be used in without affecting its physio-chemical properties.

Materials and methods

The clay sample used in present work is Wyoming MMT purchased from Podmore and Sons LTD. X-ray diffraction patterns (XRD) were recorded on a Philips diffractometer with a gas-filled proportional counter, using CuKα radiation with a step size of 0.017o and a counting time of 10 seconds, in the 2θ range of 5-80o. The infra-red spectra were recorded on a Perkin Elmer 1330 infra-red spectrophotometer. Mössbauer spectra were recorded on a Cannberra Multichannel analyzer. The source was a rhodium matrix containing 25-mCi cobalt-57 obtained from the Radiochemical Centre, Amersham. The Mössbauer spectrum is obtained by plotting the percentage transmission (or as the number of counts registered by the detector) against Doppler velocity. Photoacoustic spectra were recorded on a PAR model 6001 in the range 200-2500 nm, using carbon black as a reference. The furnase used for firing the samples was Carbolite, with a ramp rate of 5 °C/min.

The powdered samples used for Mössbauer spectra masurnment were distributed in a hole 1 mm thick in a 1 cm diameter aluminium disc. The sample was hold in a place by wrapping the disc in cellotape. Oriented samples were prepared for X-ray examination by adding 2 ml of distilled water to 0.2 g of the clay sample in a plastic vial. The mixture was dispersed by using an ultrasonic probe for minute. A thin layer from the clay suspension was deposited on a slide. The slides were then left to dry in a 60% relative humidity desiccator.

Characterizing MMT sample

The MMT samples used for this study has the following chemical composition:

Table 1. Chemical composition of the MMT samples used for this study.

Fe_2O_3	Al_2O_3	SiO_2	TiO_2	CaO	MgO	Na_2O	K_2O	Loss on ignition	Total
3.5	19.1	57.5	0.2	1.2	2.4	1.7	0.3	13.9	99.8

No attempt was made to purify the sample because structural iron can easily be oxidized by contact with water or by any mild treatment. In addition, the impurities found (quartz, feldspar and mica) do not affect the data obtained from Mössbauer spectroscopy [22].

Firing the MMT samples

The original MMT sample which has a grey color was subjected to firing treatments in a furnace, at different temperatures under air. The firing temperature ranged from 100-1000 oC, for periods of 10, 30 and 300 minutes. The sample retained the grey color up to about 300 oC, after which time the color started to change to yellow. On firing to successively higher temperature, the yellow color of the sample darkened slightly. At 700 oC the sample color was light brown, becoming darker at 1000 oC and showing the beginning of vitrification. The physical state of the sample can be described as easily broken aggregates.

Results and discussion

MMT is one of the three-layer clay minerals. Its structure consists of an octahedral layer that is sandwiched between two tetrahedral layers (Fig. 1).

http://dx.doi.org/10.29356/jmcs.v70i1.2520

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The most interesting phenomena of MMT clays is that water and other polar molecules can enter between the unit layers causing the basal spacing to expand. The basal spacing varies from 9.6 Å when no polar molecules are present to an almost complete separation in some cases.

In natural MMT clays, metal substitution is always observed to have taken place. Aluminium is often found substituted for silicon in the tetrahedral layer whereas in the octahedral layer, magnesium, iron, zinc, nickel, and lithium may substitute for aluminium. The negative charges which are generated due to this substitution are responsible for about 80 % of the total cation exchange capacity of the clay. The nature of the exchangeable cations plays an important role in the swelling of MMT. Calcium and magnesium generate hexahydrate with limited thickness of absorbed water as they take up an organised configuration. Whereas with sodium ions, the water can be absorbed up to a considerable thickness, as it does not form a hydrate. The swelling of water molecules takes place by steps during hydration thus it can take place with one, two, or three and four layers of water with basal spacings ranging from 12.4 Å to 21.4 Å respectively.

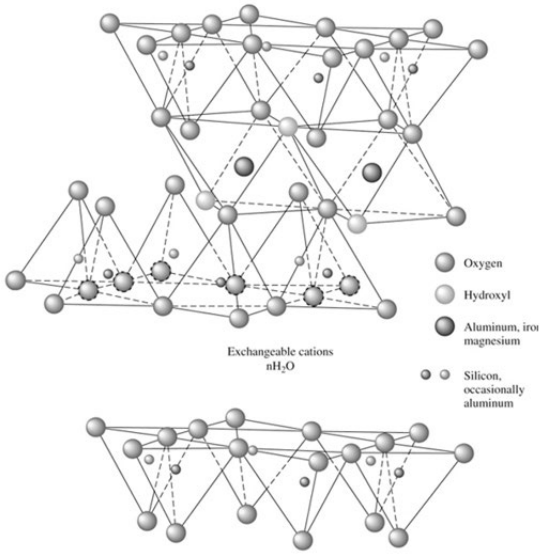

Fig. 1. Schematic presentation of MMT.

X-ray powder diffraction (XRD) of the original MMT sample

The basal spacing of the air-dried MMT sample was found to be 13 Å increasing to 17 Å on ethylene glycol treatment. Heating this sample at 120 ºC for two hours, a partial collapse was observed with a basal spacing of 12.62 Å. The collapse was completed on heating the sample at 375 ºC for 1 hour (Fig. 2).

http://dx.doi.org/10.29356/jmcs.v70i1.2520

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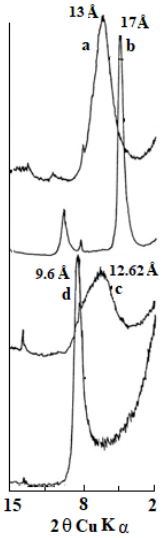

Fig. 2. X-ray powder diffraction patterns of MMT (a) untreated sample, (b) treated with EG, (c) heated at 120 ºC, (d) 375 ºC.

Infrared spectra

The main features of MMT in the IR region are the Si-O stretching and OH bending. The position of these bands were found to be at 800, 850, 880, 917, and 1040 cm^{-1} and are assigned to Fe^{3+}-OH-Fe^{3+}, Al-OH-Mg, Fe^{3+}-OH-Al, Al-OH-Al, and Si-O, respectively [23,24].

Mössbauer spectrum of the original MMT sample

Mössbauer spectrum of the original samples are shown in Fig. 3. The spectrum was fitted to two doublets corresponding to high spin iron (III) and iron (II) sites. The isomer shifts (δ) are 0.43(2) mm s^{-1} for the Fe^{3+} and 1.25(1) mm s^{-1} for the Fe^{2+} sites. The quadrupole splittings (Δ) are 0.65(2) mm $s^{-1}$for Fe^{3+} and 3.03(1) mm s^{-1} for the Fe^{2+} sites. Both iron sites are present in the octahedral layer in the clay. The small quadrupole splitting for the high spin Fe^{3+} site indicates that the octahedral site is not symmetrical, and this is confirmed from the quadrupole splitting of the high spin Fe^{2+} site. In both cases if the iron sites had been symmetrical the quadrupole splittings, would have been much smaller.

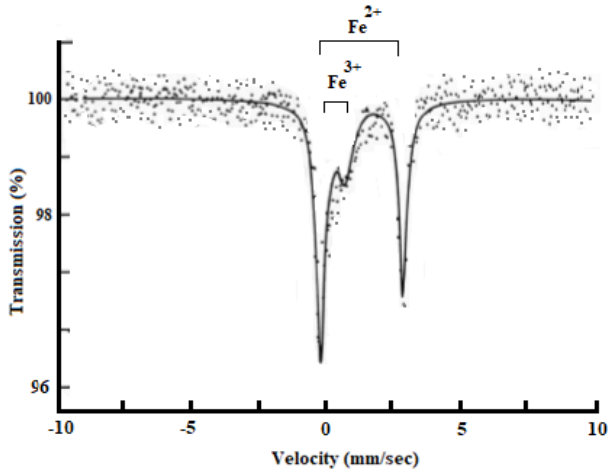

Fig. 3. Mössbauer spectrum at 77 K of MMT sample.

http://dx.doi.org/10.29356/jmcs.v70i1.2520

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Mössbauer spectra of the fired MMT samples

Mössbauer spectra of the samples fired for 30 minutes are shown in Fig. 4, 5 and 6, and the Mössbauer parameters for the fired samples are given in Table 1, 2 and 3. The first point that needs to be discussed is that the sample fired at 100 ºC for 10 minutes (see table 1) has different Mössbauer parameters to the other samples (see tables 2 and 3 and the unfired clay sample). Though it reverts back when fired at 200 ºC (see table 1). We believe this is probably due to the presence of some water or hydroxyl molecules in the sample.

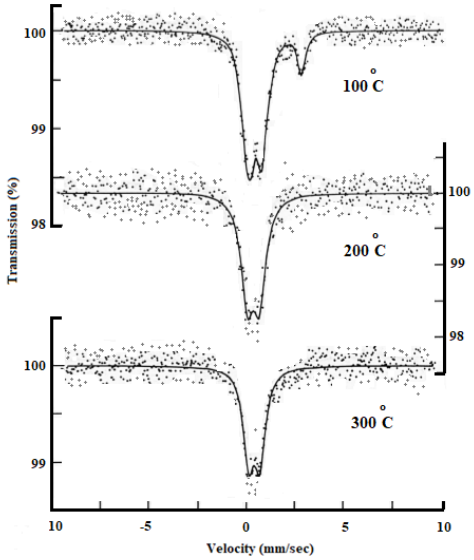

Fig. 4. Mössbauer spectra at 77 K of MMT sample fired in air at various temperatures for 30 minutes. Temperature of firing is indicated.

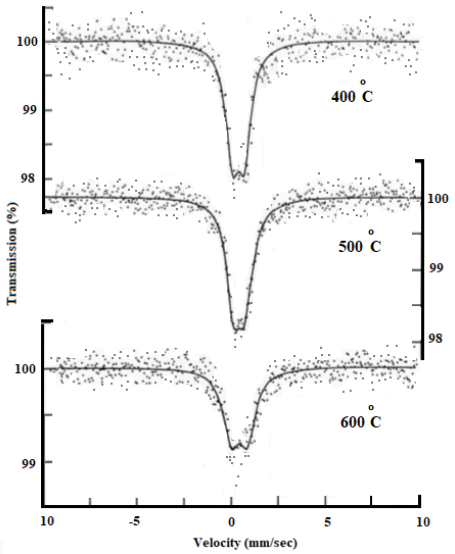

Fig. 5. Mössbauer spectra at 77 K of MMT sample fired in air at various temperatures for 30 minutes. Temperature of firing is indicated.

http://dx.doi.org/10.29356/jmcs.v70i1.2520

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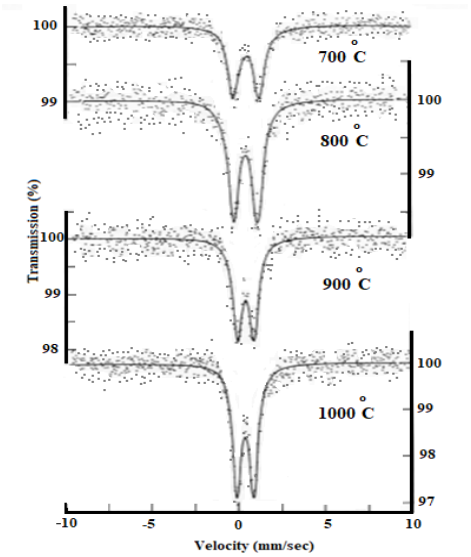

Fig. 6. Mössbauer spectra at 77 K of MMT sample fired in air at various temperatures for 30 minutes. Temperature of firing is indicated.

Table 1. The ^{57}Fe Mossbauer parameters at 77 K of the MMT sample fired for 10 minutes.

	……Fe^{2+} Parameters ……			……Fe^{3+} Parameters ……		
Temp. °C	**δ mms^{-1}**	**Δ mms^{-1}**	**Γ mms^{-1}**	**δ mms^{-1}**	**Δ mms^{-1}**	**Γ mms^{-1}**
100	1.21(5)	2.91(9)	0.30(7)	0.42(3)	0.49(4)	0.28(4)
200	1.19(4)	2.91(7)	0.42(6)	0.45(1)	0.62(1)	0.33(1)
300	-	-	-	0.43(1)	0.62(2)	0.39(2)
400	-	-	-	0.43(2)	0.63(2)	0.34(2)
500	-	-	-	0.44(2)	0.61(3)	0.44(3)
600	-	-	-	0.41(3)	0.64(9)	0.62(7)
700	-	-	-	0.48(2)	1.39(3)	0.38(3)
800	-	-	-	0.43(1)	1.52(2)	0.38(2)
900	-	-	-	0.38(1)	1.00(2)	0.35(3)
1000	-	-	-	0.37(1)	0.95(1)	0 32(1)

http://dx.doi.org/10.29356/jmcs.v70i1.2520

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Table 2. The ^{57}Fe Mossbauer parameters at 77 K of the MMT sample fired for 30 minutes.

	…….Fe^{2+} parameters ……			**……Fe^{3+} parameters ……**		
Temp. ºC	**δ mms^{-1}**	**Δ mms^{-1}**	**Γ mms^{-1}**	**δ mms^{-1}**	**Δ mms^{-1}**	**Γ mms^{-1}**
100	1.27(2)	2.98 (3)	0.24(3)	0.45(1)	0.62(1)	0.34(1)
200	-	-	-	0.44(2)	0.63(3)	0.38(3)
300	-	-	-	0.41(1)	0.59(2)	0.34(2)
400	-	-	-	0.45(2)	0.65(3)	0.43(3)
500	-	-	-	0.47(1)	0.60(3)	0.47(3)
600	-	-	-	0.47(2)	0.88(4)	0.58(4)
700	-	-	-	0.47(1)	1.48(2)	0.38(2)
800	-	-	-	0.46(1)	1.37(2)	0.39(2)
900	-	-	-	0.40(1)	0.96(2)	0.34(2)
1000	-	-	-	0.38(1)	0.98(1)	0.32(1)

Table 3. The ^{57}Fe Mossbauer parameters at 77 K of the MMT sample fired for 300 minutes.

	…….Fe^{2+} Parameters ……			**……Fe^{3+} Parameters ……**		
Temp. ºC	**δ mms^{-1}**	**Δ mms^{-1}**	**Γ mms^{-1}**	**δ mms^{-1}**	**Δ mms^{-1}**	**Γ mms^{-1}**
100	-	-	-	0.41(1)	0.64(2)	0.36(1)
200	-	-	-	0.42(1)	0.65(1)	0.39(1)
300	-	-	-	0.39(1)	0.60(2)	0.38(2)
400	-	-	-	0.41(1)	0.61(3)	0.43(3)
500	-	-	-	0.43(1)	0.65(2)	0.50(2)
600	-	-	-	0.46(1)	1.38(2)	0.40(1)
700	-	-	-	0.43(1)	1.49(1)	0.40(1)
800	-	-	-	0.41(1)	1.36(1)	0.41(1)
900	-	-	-	0.36(1)	0.96(1)	0.35(1)
1000	-	-	-	0.33(1)	0.93(1)	0.37(1)

http://dx.doi.org/10.29356/jmcs.v70i1.2520

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It is obvious from the parameters presented in Table 1, 2 and 3 that Fe(II) can be readily oxidized to Fe(III). In the sample fired for 10 minutes a partial oxidation of Fe(II) at both 100 and 200 ºC is apparent, and the oxidation process is completed at 300 ºC. When the sample was heated for 30 minutes, the Fe(II) was only found at 100 ºC and had all oxidized at 200 ºC. In the sample fired for 300 minutes, all the Fe(II) has been oxidized at 100 ºC. From these results, it is clear that transformations induced in the MMT samples by firing are dependent on the time and temperature of firing. As there is no formal change in the Mössbauer parameters of the Fe(III) site when the samples were fired between 100 to 500 ºC this is good evidence that on oxidation, the Fe(II) converts to Fe(III) on the same site and that both the Fe(II) and Fe(III) sites are the same in the MMT samples. Although firing around this range of temperature causes the interlayer, pore and physically bound unstable water to be driven off [25], this latter process has no effect on the environment of the structural iron. The main changes in the Mössbauer parameters of the Fe(III) sites occurred upon firing from 600 ºC up to 1000 ºC. The isomer shift decreases gradually with increasing temperature of firing, due to the de-hydroxylation of the structure. The process of de-hydroxylation, which is the release of the hydroxyl groups coordinated to the structural Fe(III) cations, causes a decrease in the coordination number of iron. This leads to an increase in the degree of covalency in the bond, which in turn has the effect of removing electron density from the iron outer orbitals.

The quadrupole splitting of the Fe(III) site increases in the MMT samples fired above 600 ºC up to a maximum around 700 ºC for the samples fired for 30 and 300 minutes, indicating an increase in distortion of the lattice as the temperature was raised. The maximum value of the quadrupole splitting was found in the sample fired at 700-800 ºC (around 1.5 mms^{-1}), then it started to fall to a value around 0.9 mms^{-1}. The slow decrease in the quadrupole splitting at high temperature is due to the gradual recrystallization of the disordered structure [26].

A slight increase in the linewidth (Γ) of Fe(III) values of the fired samples from that of the original sample (Γ = 0.30 mms^{-1}) was found, suggesting that either more than one iron site occurs (possibly due to different orientations of the hydroxyl ligands) or that there is some slight distortion present on some of the Fe(III) octahedra.

The firing process can be explained by two terms, oxidation and de-hydroxylation. The main process below 600 ºC is the oxidation of Fe(II), and above 600 ºC the main process is de-hydroxylation of the lattice. The mechanism proposed [27,28] for Fe(II) oxidation in the presence of environmental oxygen is:

$$4Fe^{2+} + 4OH^- + O_2 \longrightarrow 4Fe^{3+} + 4O^{2-} + 2H_2O$$

and in the absence of the oxygen:

$$4Fe^{2+} + 4OH^- \longrightarrow 4Fe^{3+} + 4O^{2-} + 2H_2$$

The second reaction is dominant at low temperatures, even in the presence of environmental oxygen, since oxygen molecules are too big to penetrate the lattice. Firing to a higher temperature causes the decomposition of the hydroxyl groups to an oxygen ion and water in the neighborhood of a vacancy [29].

$$OH^- + OH^- \longrightarrow H_2O + O^{2-}$$

Photoacoustic spectroscopy

Photoacoustic spectroscopy investigations on the MMT sample showed that there are two bands at 1400 and 1910 nm correspond to the water of hydration (Fig. 7). However, those two bands were reported at 1380 and 1880 nm previously [30]. The spectra also exhibited a band at 2200 nm corresponding to the structural hydroxyl groups.

The spectra of the fired sample showed a decrease in the intensity of the water bands at 1400 and 1910 nm. This decrease started on firing at 100 ºC and continued up to about 700 ºC. The remaining water was observed up to 700 ºC, due to the short time of firing, or it could be due to rehydration on cooling. The intensity of the 2200 nm band, which is attributed to the structural OH remained unchanged up to 600 ºC.

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However, the intensity of this band started to decrease on firing higher than 600 °C. This is in keeping with lattice de-hydroxylation that starts at 600 °C.

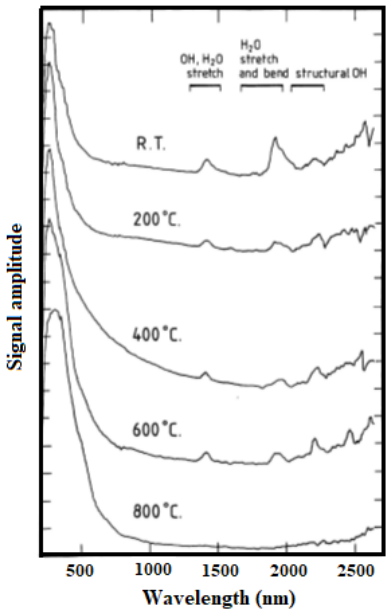

Fig. 7. Photoacoustic spectra of montmorillonite sample fired in air at various temperatures. Temperature of firing is indicated.

Conclusions

Wyoming MMT samples undergoes a color and structural transformation upon firing. The process depends on the time and temperature to which the clay was fired. Mössbauer studies showed that the original samples contain both Fe(II) and Fe(III). The oxidation of Fe(II) has been shown to be complete by firing to about 200 °C. The main changes in the structure appeared upon firing above 600 °C due to the de-hydroxylation of the clay lattice leading to a decrease in the coordination number of the iron. The decrease in the coordination number causes an increase in the degree of covalency, which has the effect of removing electron density from the iron outer orbitals. The oxidation of iron (II) is explained by the equation:

$$4Fe^{2+} + 4OH^{-} \longrightarrow 4Fe^{3+} + 4O^{2-} + 2H_2$$

The oxidation process gives ferric ions coordinated by five oxygen atoms and one hydroxyl group $Fe^{3+}(O_5\ OH)$.

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