



УДК 543.544

Structural Studies of Natural Montmorillonites

AlSawalha M.¹, Obra E.¹, Roessner F.²

¹*Department of Chemical & Process Engineering Technology, Jubail Industrial College, Jubail Industrial City, Kingdom of Saudi-Arabia*

²*Institute of Chemistry, University of Oldenburg, Oldenburg, Germany*

Поступила в редакцию 12.09.2016 г.

Four different natural Jordanian Montmorillonites: diatomite, zeolite, bentonite, and kaolinite (white and red kaolinite) without any further purification or treatments were characterized by FTIR and SEM/EDS techniques. FTIR validated the existence of silanol and hydroxyl group bridges on the clay surface, while SEM verified the chemical composition SEM/EDS and the morphological structure of the Jordanian clays. The results confirmed the presence of silanol and hydroxyl links on the samples surface and the existence of some ions on the natural Montmorillonites.

Keywords: Natural Montmorillonites, SEM/EDS, Chemical composition, Clay

Исследование структуры природных монтмориллонитов

АльСавальха М.¹, Обра Е.¹, Ресснер Ф.²

¹*Department of Chemical & Process Engineering Technology, Jubail Industrial College, Jubail Industrial City, Kingdom of Saudi-Arabia*

²*Institute of Chemistry, University of Oldenburg, Oldenburg, Germany*

Методами ИК-Фурье-спектроскопии и сканирующей электронной микроскопии исследованы образцы четырех различных природных монтмориллонитов (Иордания): диатомит, цеолит, бентонит и каолинит (белый и красный каолинит) без какой-либо очистки или обработки. С помощью ИК-Фурье-спектроскопии подтверждено наличие силанольных и гидроксильных групп, образующих мостики на поверхности глинистого материала, методом СЭМ установлен химический состав и морфологическая структура иорданских глин. Результаты подтвердили наличие силанольных и гидроксильных связей на поверхности образцов, а также наличие некоторых ионов в природных монтмориллонитах.

Ключевые слова: природные монтмориллониты, СЭМ/ЭДС, химический состав, глины

Introduction

Clay is a naturally occurring, inorganic component of most soils. It is made up of tiny particles less than 0.002 mm in diameter. Chemically, clays are aluminosilicates $[Al_4Si_4O_{10}(OH)_8]$ and carry negative charges. Some of the most important traditional applications of aluminosilicates are in ceramics, paper, pigment, plastics, drilling fluids, foundry pendants, chemical carriers, liquid barriers, decolorization, and catalysis. Clays and clay minerals have been mined since the Stone Age; today they are among the most important minerals used also by manufacturing and environmental industries

In many industrial applications, the surface properties and reactivity of clays are of bigger importance than their bulk composition. Changes in the spectra of molecules adsorbed on the clay surface provide direct information on the mechanism and sites of adsorption. Hence, each material will bear a different spectrum and, therefore, FTIR analysis can be used in identifying its sites. In addition, the size of the spectral peaks provides information on the composition of the material[1].

SEM, on the other hand, uses beam of high-energy electrons that produces different signals at the surface of a solid material. These signals provide information on the morphology, crystalline structure of the material and the chemical composition of the sample.

Natural clays, such as kaolinite, bentonite, palygoskite, volkonskoite and elite and black mold are widely distributed in Jordan [2]. An understanding of the properties of Jordanian clays will help in describing its behavior when subjected to certain catalytic reactions and adsorption activities[3, 4].

It is the aim of this study to study the composition and properties of the natural Jordanian clays using Fourier transform infrared (FTIR) and scanning electron microscopy (SEM). Some FTIR studies can be found in the literature but only limited SEM analyses were done on natural Jordanian clays.

Experimental

Materials and Procedures. For this study different natural Jordanian samples were considered: diatomite, zeolite, bentonite and kaolinite (white and red kaolinite). Bentonite samples were collected from Al Azraq region, which is located approximately 120 km northeast of Amman; kaolin samples were taken from south Jordan, Batn el-Ghoul, Al-Mudawwara; diatomite samples were gathered in separate horizon of Azraq Mud flat area approximately 110km northeast of Amman: and zeolite samples were collected from at Jabal Aritayn (30km NE of Azraq town). The chemical compositions of these clays are provided in Table 1.

Table 1. Chemical composition of Jordanian samples containing zeolite, bentonite, white kaolinite, red kaolinite and diatomite [1]

Oxides (%wt.)	Zeolite	Bentonite	White Kaolinite	Red Kaolinite	Diatomite
SiO ₂	42.0	55.7	48.0	47.6	72.0
Al ₂ O ₃	12.8	20.1	36.3	24.9	11.4
Fe ₂ O ₃	12.1	1.5	1.0	6.1	5.8
MgO	10.1	3.5	0.3	1.0	-
CaO	8.5	2.1	0.1	0.5	1.5
Na ₂ O	4.0	0.1	0.1	0.8	7.2
K ₂ O	0.8	2.4	1.8	2.3	-
TiO ₂	-	2.5	0.1	0.7	-

Methodology. Characterization of natural Jordanian clays by FTIR measurement and the analysis of spectra were done by using a Shimadzu IR Prestige-21/FTIR-8400S spectrophotometer through the wave number range from 400 to 3900 cm⁻¹ using, the KBr pellet technique. The spectra were summarized by using the FTIR software. The data interval provided by the instrument for a resolution of 4 cm⁻¹ is 1 cm⁻¹. The chemical composition and morphology were investigated by scanning electron microscope (SEM/EDS) at different KV magnifications, using a JEOL JSM-6390A model.

Results and discussion

FTIR Results. Based on the FTIR spectra, the following were observed.

Diatomite. The sample surface contains silanol groups that are spanned over the structure of the silica. Zhuravlev [5] reported that the diatomite surface is covered by OH groups and oxygen bridges, which act as adsorption sites that may be characterized by taking into account: i. the chemical activity of the surface (i.e. this activity depends on the concentration and the distribution of different types of OH groups and on the existence of siloxane bridges), and the porous structure of the diatomite. Moreover, it was proved that the silanol groups are more effective than the siloxane groups in forming hydrogen bonds, which can only act as proton acceptors. The silanol groups on the diatomite surface are hydrophilic in nature. This is due to the electron density, which becomes delocalized from the O–H bond to the neighboring Si–O bond. Zhuravlev [5] showed that there are possibilities that the silanol groups has the ability to form strong hydrogen bonds with water molecules or other molecules.

The main absorption bands for the sample reached at 3740 cm^{-1} correlated to the free group of silanol (Si–OH) while the bands at 1088 and 1026 cm^{-1} related to the siloxane (Si–O–Si). Furthermore, the peaks at 920 , 680 and 610 cm^{-1} were due to Si–OH stretching of silanol group and SiO–H vibration, respectively. The peak of stretching Si–OH bond resulted in a band at 3750 cm^{-1} .

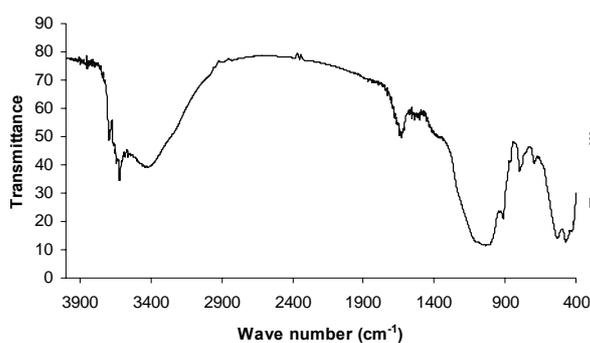


Fig. 1. The infrared spectra of the studied Jordanian Diatomite sample

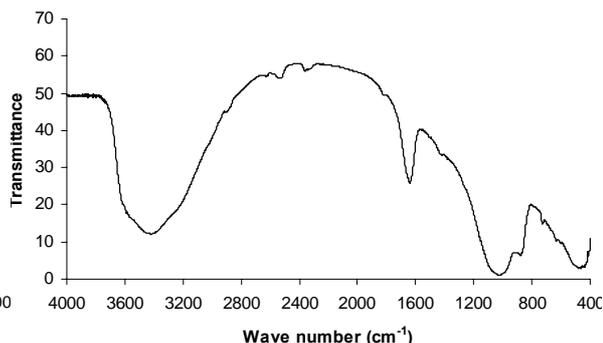


Fig. 2. The infrared spectra of the studied Jordanian Zeolite sample

Zeolite. Zeolites are three-dimensional framework aluminosilicates with cavities and channels hosting various cations, molecules and water molecules. Using FTIR spectroscopy Korkuna [6] observed bands at 3620 cm^{-1} assigned to acidic hydroxyls Si–O (H)–Al, a band at 3400 cm^{-1} due to the vibration of the bonds O–H---O, a band at 1620 cm^{-1} linked to deformation vibration of absorbed water and a band at 1020 cm^{-1} due to the asymmetric valence vibrations in tetrahedra SiO_4 .

Investigated sample showed that the peaks in region of $3460\text{--}3620\text{ cm}^{-1}$ can be caused by the O–H vibrations in various environments. Therefore, the band at 3720 cm^{-1} is brought about by the terminal silanol–OH, the band at 3540 cm^{-1} by the Si–OH–Si(Al) bridge, and the bands at 3565 and 3475 cm^{-1} by the hydrogen bonded as Si(Al)–OH. Different water absorption broad bands appeared at 3400 and 3200 cm^{-1} indicating the different types of bonding and locations for the water molecules. Hence, the high frequency band at 3450 cm^{-1} could be attributed to some parts of water within the sample. It has been reported also that the bending vibration of H_2O is found at 1650 cm^{-1} , which shifted to higher frequency as compared to molecular water [7].

Bentonite. To investigate the structural properties of bentonite, FTIR analyses were carried out in the range of $400\text{--}3900\text{ cm}^{-1}$. The infrared spectra shown in Fig. 3 indicated

the existence of absorption bands corresponding to Si–O, Al–O and Ca–O vibrations (3600 , 1600 , 1383 , 1052 , 890 , and 525 cm^{-1}). It was found [8], that these bands corresponds to Al–OH–Al, bending vibrations as observed at 918 cm^{-1} . The (Si–O) bands are strongly evident in the silicate structure and can be readily recognized in the infrared spectrum by the very strong absorption bands in the 1100 – 1000 cm^{-1} regions, while the bands at 525 and 468 cm^{-1} are due to Al–O–Si and Si–O–Si bending vibrations, respectively. The band at 620 cm^{-1} is due to coupled Al–O and Si–O out-of-plane vibrations. The IR band at 3437 cm^{-1} correspond to OH frequencies (silanol group (Si–O–H)) while the IR band at 1638 cm^{-1} represents H–O–H bending vibration of water [8, 9].

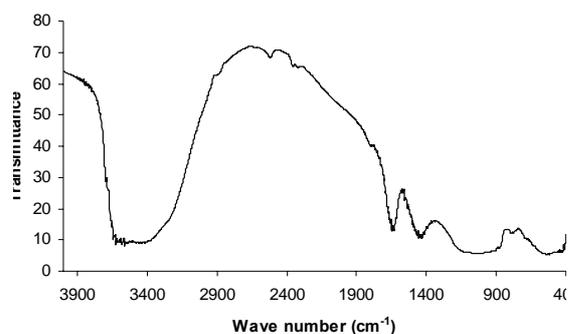


Fig. 3. the infrared spectra of the studied Jordanian Bentonite sample

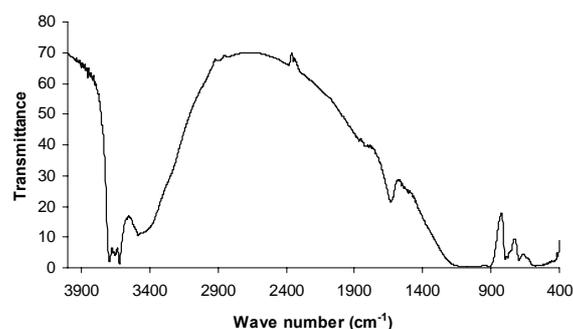


Fig. 4. The infrared spectra of the studied Jordanian Kaolin sample

Kaolin. Kaolinite is a common clay mineral with general formula: $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$. It is composed of a two-layer arrangement, where the geometries around aluminum and silicon central atoms are octahedral and tetrahedral, respectively [10, 11]. From FTIR results, four different vibrational regions can be used to describe the properties of kaolinite sample. These are: the O–H stretching (3800 – 3600 cm^{-1}), the Si–O between (1120 – 1000 cm^{-1}), the O–H bending (930 – 900 cm^{-1}) and the SiO_2 bending (430 – 520 cm^{-1}) regions. A shoulder at 1160 cm^{-1} indicates on the presence of quartz [12].

SEM Results

The electron diffraction spectra (EDS) confirms the presence of the following ions on the clay:

- 1) Zeolite – silicon, aluminum, magnesium, calcium, iron, and titanium;
- 2) Bentonite – silicon, aluminum, calcium, iron, and potassium;
- 3) White kaolinite – silicon, aluminum, iron, titanium and potassium; and
- 4) Red kaolinite – silicon, aluminum, iron and potassium.

These results are consistent with the chemical composition data in Table 1. Based on the x-ray spectra of the four clays from Fig. 5, bentonite has the highest silicon signal followed by red kaolinite, zeolite and white kaolinite; red kaolinite has the highest aluminum signal followed by white kaolinite, bentonite and zeolite; zeolite has the highest iron signal followed by bentonite, red kaolinite and white kaolinite; and red kaolinite has the highest potassium signal followed by bentonite, white kaolinite and zeolite.

Figures 5b and 5d are consistent with the electron diffraction results for kaolinites by Rajkumar [13]. The x-ray spectra showed the presence of dominant elements such as aluminum, titanium, iron, magnesium, potassium and silicon.

Figure 5c is consistent with the x-ray spectra results of Naswir [14]. It was found out, that the biggest constituent composition of bentonites are SiO_2 with a percentage composition range from 44.11 to 64.16%, and Al_2O_3 with a percentage composition range from 18.75 to 39.26% as shown in Table 2.

Figures 6 to 9 illustrate the morphology of Jordanian clays. Based on the SEM micrographs of the four Jordanian clays, zeolite showed typical irregular shapes which are randomly arranged tubular and cubic particles; white kaolinite revealed irregular platelets which have ragged edges and form sub-rounded flakes with less of the tubular particles and more of the cubic particles and with rough and angular edges; bentonite showed randomly arranged particles with more of the tubular ones in the form of elongated flakes; and red kaolinite showed almost the same morphology as the white kaolinite.

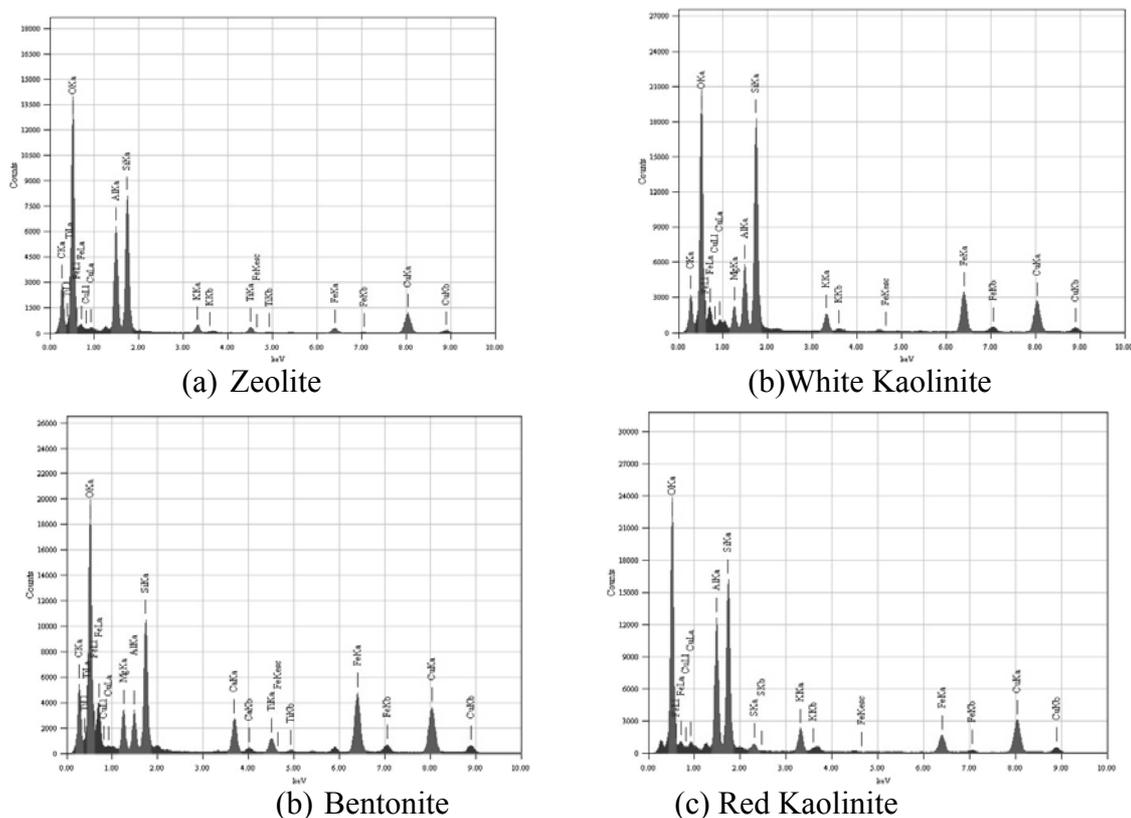


Fig. 5. SEM-EDS of: a) Zeolite, b) White Kaolinite, c) Bentonite and d) Red Kaolinite

Table 2. The Composition of the Building Blocks of Bentonite [6]

Compound	Sample of Bentonite				
	B.BT	B.P	B.T.R	B.P.P	B.P.R
SiO ₂	44.11	50.92	46.32	64.16	52.63
Al ₂ O ₃	33.61	31.09	39.26	20.22	18.75
TiO ₂	0.66	0.70	0.08	0.20	0.17
CaO	0.01	-	0.08	0.10	0.01
MgO	0.19	0.31	0.06	1.30	1.45
K ₂ O	0.04	0.75	0.11	0.18	0.13
Na ₂ O	-	0.06	0.11	0.03	0.11
FeO	2.22	4.35	1.88	3.53	3.13
CuO	3.85	1.49	3.03	2.07	2.82
C	14.24	8.11	8.31	7.26	19.26

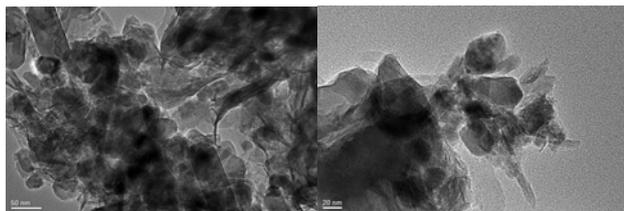


Fig. 6. Zeolite at 50k and 80k magnification

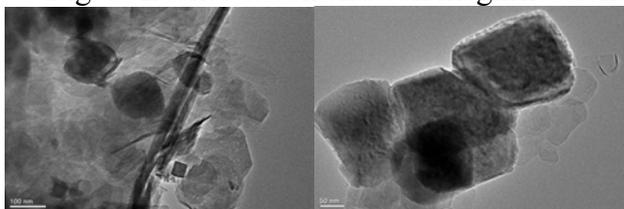


Fig. 7. White kaolinite at 30k and 40k magnification

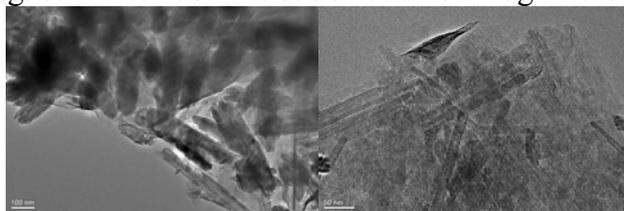


Fig. 8. Bentonite at 20k and 50k magnification

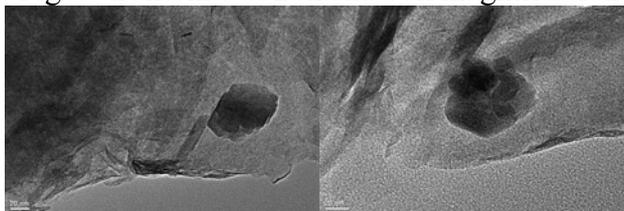


Fig. 9. Red Kaolinite at 80k and 100k magnification

Conclusion

FTIR Results. The FTIR results confirm the sites where silanol- and hydroxyl-groups can be found as reported in the literature while SEMD results verify the existence of different ions as reported in the analysis. SEM results also show the morphological structure of the four clays. The results indicate a good correlation on the clay properties found in the literature.

Other recommendations. To have a better understanding of the behavior of the Jordanian natural Montmorillonites, the samples will be subjected to other characterization techniques such as XRD, swelling index and catalysis adsorption. The Jordanian clays will also be compared with the local Saudi clays to see the possibility of utilizing the local Saudi clays as alternative clays where the Jordanian clays are being used. However, because of the limited SEM studies made on natural Jordanian clays, additional characterization techniques such as XRD can be conducted.

The authors would like to acknowledge Dr. Abdulaziz Bagabas, for his supervision in performing the SEM analysis in the KACST facilities. This recognition is offered to those who helped in the SEM analysis: Mr. Abdulmajeed Khalifa, Mr. Abdulrahman Ghaib and Mr. Sultan Al-Bishi.

References

1. Markovich R.J., Pidgeon C., *Pharmaceutical Research*, 1991, Vol. 8, No 6, pp. 663-675.
2. Khoury H.N., *Jordan Journal of Earth and Environmental Sciences*, 2014, Vol. 6, No 3, pp. 1-10.
3. Alsawalha M., Roessner F., Novikova L., Bel'chinskaya L., *World Academy of Science, Engineering and Technology*, 2011, Vol. 5, No 7, pp. 319-323.
4. Bel'chinskaya L.I., Strel'nikova O.Yu., Novikova L.A., Roessner F. et al., *Protection of Metals*, 2008, Vol. 44, No 4, pp. 390-393.
5. Zhuravlev L.T., *Colloids Surfaces A: Physicochem. Eng. Aspects*, 2000, Vol. 5, No 173, pp. 1-38.
6. Korkuna O., Leboda R., Skubiszewska-Zieba J., Vrublevs'ka T. et al., *Microporous and Mesoporous Materials*, 2006, Vol. 87, pp. 243-254.
7. Prasad P.S.R., Shiva Prasad K., *Microporous and Mesoporous Materials*, 2007, Vol. 100, pp. 287-294.
8. Yousef R.I., Tutunji M.F., Derwish G.A.W., Musleh S.M., *Journal of Colloid and Interface Science*, 1999, Vol. 216, pp. 348-359.
9. Wang S., Nan Z., Li Y., Zhao Z., *Desalination*, 2009, Vol. 249, pp. 991-995.
10. Zaitan H., Bianchi D., Achak O., Chafik T., *Journal of Hazardous Materials*, 2007, Vol. 153, pp. 852-859.
11. Qtaitat M.A., Al-Trawneh I.N., *Spectrochimica Acta Part A*, 2005, Vol. 61, pp. 1519-1523.
12. Saikia N.J., Bharali D.J., Sengupta P., Bordoloi D. et al., *Applied Clay Science*, 2003, Vol. 24, pp. 93-103.
13. Rajkumar K., Ramanathan A.L., Behera P.N., *Journal Geological Society of India*, 2012, Vol. 80, pp. 429-434.
14. Naswir M., Arita S., Salni Marsi, *Journal of Clean Energy Technologies*, 2013, Vol. 1, No 4, pp. 313-317.

AlSawalha Murad - Assistant professor, department of Chemical & Process Engineering Technology, Jubail Industrial College, Jubail Industrial City, PO Box 10099, 31961, Kingdom of Saudi-Arabia, Murad_s@jic.edu.sa

Edwin Obra - Lecturer, Department of Chemical & Process Engineering Technology, Jubail Industrial College, Jubail Industrial City, Kingdom of Saudi Arabia, obra_e@jic.edu.sa

Frank Roessner - Prof. Dr., Dr. h.c. Chemical Technology II Institute of Pure and Applied Chemistry Faculty of Mathematics and Natural Sciences University of Oldenburg, Oldenburg, Germany, e-mail: frank.roessner@unioldenburg.de