Analytical Study for Physicochemical Characteristics of Bentonite Clay in Libya

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Abstract: This study highlights the mechanism of formation for Bentonite clay surface properties. It investigates specific gravity and the influence of physicochemical characteristics on clay stability of structural forces on adsorbed water molecules. In particular, it describes the chemical composition, as well as cation exchange capacity (CEC). Bentonite clay is collected from the Murzuq city located 1150 km south of Tripoli i.e. southernmost town of Libya. The CEC value is leached by 500ppm Ca^{+2} at pH=8 equaled 84.5 mmoles/kg. While at pH=2, the value is (20.5 mmoles/kg). The leaching process is carried out by 500ppm K^{+} using flame emission photometer. The CEC value at pH =8 for sample is 91.5 mmoles/kg. Also the specific gravity is found to be 2.597. This value is in agreement with the obtained standard values for Wyoming (USA). The % M_xO_y of the clay is calculated by gravimetric method as follows: SiO_2, 53.75; Al_2O_3, 21.46; Fe_2O_3, 1.4; CaO, 0.97; MgO, 2.13, and agreed with the XRF analysis as follows: SiO_2, 54.93; Al_2O_3, 21.46; Fe_2O_3, 1.71; MgO, 3.18 ; CaO, 0.81; Na_2O, 5.48; K_2O, 0.54; TiO_2,0.32. The results are adequately approximate and reasonable for both methods. The percent is very limited for trace elements Pb, Cr, Cd, Cu, Fe, and Zn. In the sample, it is about 0.21%. The result of XRD analysis (intensities) for sample is presented as follows: 50% quartz, 50% kaolinite, 5% Analcine, 7.5% Illite, 5% Natrolite, 10% Nontronite, 7% Montmorillonite. The formula calculation depends on the purity of clay and consequently the structural formula for Libyan Bentonite is: $K_{0.094}Na_{1.45}Ca_{0.118}\ (Al_{2.92}Fe_{0.175}Ti_{0.033}Mg_{0.646})^{VI}(\ Al_{0.52}Si_{7.48}\ )^{IV}O_{20}(OH)_4$

Keywords: Physicochemical properties, XRD, XRF, FT-IR, Structural formula.

INTRODUCTION

Bentonite clay is an absorbent aluminum phyllosilicate. It is generally impure clay consisting mostly of montmorillonite. It is a dual layered, dual-dimensional mineral. These minerals give it a layer of cards that looks like crystalline packets and called platelets. Bentonite is a geological extract found freely in natural state. There are some nomenclatorial problems with the classification of bentonite clays. Bentonite usually forms from weathering of volcanic ash, most often in the presence of water, (Mitchell, 1993; Lagaly, 1995). However, the term bentonite, as well as similar clay called Tonsteins (Kaolin) can be used for clay beds of uncertain origin. Bentonite may also contain Feldspar, Biotite, Kaolinite, Illite, Cristobalite, Pyroxene, Zircon, and crystalline quartz. Bentonite is greasy and soap like to the touch. Freshly exposed, bentonite is white to pale green or blue and, with exposure, darkens in time to yellow, red, or brown, (Navarotsky,1994; Wright, 2003; Admis, 2005; Al-Ani, 2008). Libya has only one regional factory in Benghazi (Al-Joewf Company) that is produces 100,000 tons yearly. Libya needs 1.6 Million tons of bentonite yearly. To meet this need requires importing this substance from other countries to use it in different industrial fields, especially in drilling mud for oil and gas wells. However, some bentonite clay of Libyan origin called (as a common name) ***"White Mud"*** is found to be effective without any modification.

EXPERIMENTAL METHODS

Materials: The bentonite clay, Atomic Absorption Spectrophotometer, GBC Analysis, Model GBC 932, (Austria), FT-IR Spectrometer, (VARIAN 660-IR,USA), Flame Emission Photometer, (PFP7, JENWAY, Germany), (used for determination Na and K), XRF, Bruker AXS, (Model S-8 TIGER, 2010, Germany), XRD, Bruker AXS, (Model D-5005 TIGER, 2010, Germany), Mixer Rotating, (Edmund

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Buhler, 400 rpm, Mot./min,(Germany), and pH Meter, while concentrated HNO_3 manufactured by Carlo ERBA Lab, Italy, Tripoli University. All materials stated above are used as received without any further purification.

Digestion Method: Weigh 1.0 gram of dry sample in conical flask. Added 5 ml conc. HNO_3 and covered with watch glass, Bring to slow boil on hot plate and evaporate not to dry for 30 minute. Add 10 ml conc. HNO_3, cool flask between additions evaporate on a hot plate to remove all HNO_3 before continuing treatment until all elements in sample dissolved and converted metals in the sample to nitrate completely except silica insoluble . Cooled and diluted to about 50 ml with distilled water and heat to almost boiling, then cooled at room temperature. After that, filtered and transferred to a volumetric flask 100 ml, finally it diluted to the mark, (Greenberg, *et al*, 2005).

Gravimetric Analysis

Determination of the Weight of Silica (SiO_2)

(a) Weigh 5.0gm of sample in beaker. Add 10ml of conc. HNO_3, and cover the beaker with a watch glass. Allow the acid to run down the lip of the covered beaker. After the chemical action has subsided, lift the cover. Add 5ml of acid to complete reaction. Then evaporate not to dry on hot plate for 30min. Add 50ml of distilled water. Stir the mixture with glass rod, (Welcher, 1975).

(**b) Filtration:** While preparing a mixture of hot filter through medium-texture filter paper wash dish and residue (**SiO_2**) with a minimum volume of distilled water. Save all washing to use it for later analysis.

(c) Ignition: Transfer the two filter paper and residues to platinum or porcelain crucible, dry on hot plate at 110°C, and ignite at 1000°C to constant weight. Too rapid heating may form black silica, cool in desiccators weigh, and repeat ignition and weighing until constant weight is attained. Record the weight of crucible and contents.

Determination of the Weight of $(Fe, Al)_2O_3$

(a) To the filtrate reserved in accordance with step (b) above of procedure silica should have a volume of 200 ml, and heated to boiling for 15 mins. Then treat with 10ml of NH_4OH until the brown or sometimes white color precipitate appears.

(b) Filtration: Filter and wash, two times for small precipitate to four times for large. Save all washing to use it for later analysis.

(c) Ignition: Transfer the two filter paper and residues to platinum or porcelain crucible, dry on hot plate at 110°C, and ignite at 1000°C to constant weight. Too rapid heating may form black metal oxide, cool in desiccators weigh, and repeat ignition and weighing until constant weight is attained. Record the weight of crucible and contents (Fig. 1).

Determination of the Weight of CaO

(**a)** To the filtrate reserved in accordance with procedure of $(Fe, Al)_2O_3$ having a volume 300ml, heat to boiling and add a few drops of methyl red indicator and 30ml ammonium oxalate (50g per liter). Heat the solution from 70°C to 80°C, and add NH_4OH (1:1) drop wise, until the color change from red to yellow. The precipitate is calcium oxalate (white). Allow the solution to stand without further heating for (1h), (Fig. 2).



Fig.1. Precipitation of $(Fe, Al)_2O_3$



Fig.2. Precipitation and Filtration of CaO

(b) Filtration: Filter and wash moderately with water. Save all washing to use it for later analysis.

(c) Ignition: Transfer the two filter paper and residues to platinum or porcelain crucible, dry on hot plate at 110°C, and ignite at 1000°C to a constant weight. Too rapid heating may form black calcium oxide, cool in desiccators weigh, and repeat ignition and weighing until constant weight is attained. Record the weight of crucible and contents, (Welcher, 1975).

Determination of the Weight of MgO

(a) To the filtrate reserved in accordance with procedure of CaO having a volume 400ml, heat to boiling, then add 20ml Na_2HPO_4 (100g per liter), and add 10ml NH_4OH drop by drop, cool and transfer it to magnetic movement to precipitate for 1h. Allow the solution to stand without further heating for (2h). Filter and wash it with water **(**Fig. 3**).**

(b) Ignition: Transfer the two filter paper and residues to platinum or porcelain crucible, dry on hot plate at 110°C, and ignite at 1000°C to constant weight. Too rapid heating may form black magnesium oxide, cool in desiccators weigh, and repeat ignition and weighing until constant weight is attained. Record the weight of crucible and contents.

Specific and Selective Precipitation

Principle: There are many important advantages in the use of organic reagents over inorganic reagents when used as precipitants for inorganic substances. Among these are the following: (**a**) It is often possible to attain a degree of selective not possible with an inorganic reagents; (**b**) Many organic reagents are acidic and therefore improve selectivity in precipitation reactions that can be achieved by a careful control of the hydrogen ion concentration;(**c**) The precipitates formed in reactions of organic reagents with inorganic ions are often extremely insoluble and frequently very high in molecular weight. This method is useful in many important analytical separations, like Al from Be, Mg, from alkaline and alkaline earth, at pH (4.5-5). The reagents are 0.01M Oxine (8-Hydroxyquinoline), Chloroform and 2.0N Acetic acid**,** (Welcher, 1975).



Fig.3. Precipitation of MgO

Separation of Al by Organic Solvent

(a) Procedure: Weight 3.0gm of sample in beaker, add 10ml of conc. HNO_3, and cover the beaker with a watch glass, allowing the acid to run down the lip of the covered beaker. After the chemical action has subsided, lift the cover; add 5ml of acid to complete digestion. Then, carefully evaporate to dry on hot plate for 30minute. Add 50ml of distilled water, stir the mixture with glass rod, and cooled at room temperature**.** After that make filter using filtration funnel and filter paper (40mm). Finally, the filtrate is saved in clean beaker to use later for the analytical separation, (Skoog, and *et al* 2000; Harris, 2007).

(b) Extraction: Weigh clean and dry beaker. Then extract it immediately with chloroform $CHCl_3$ using separatory funnel. Transfer extracted sample to separation funnel and add 10ml of 0.01M Oxine, followed with 20ml chloroform, close it with stopper. Shake the funnel at least 5 times. Open tap or lift the stopper to remove entrapped air, and then collect the organic layer in a beaker. Transfer the extracted layer to hot path water for drying at 70°C to evaporate and remove the chloroform (Repeat the operation three times until all the precipitation of Al is completed from aqueous phase). Finally, weigh the beaker and precipitation, (Fig. 4).

Determination of the Specific Gravity

Procedure: The specific gravity is determined by density bottle method. It is most suitable for determining specific gravity. The mass (80g) $\mathbf{M_1}$ of empty dry bottle is first taken. A 40g of sample is taken and kept it in bottle and the mass (120g) $\mathbf{M_2}$ is taken. The bottle is then filled with distilled water (or kerosene), gradually and removing the entrapped air either by applying vacuum or shaking the bottle. The mass (149.60g) $\mathbf{M_3}$ of the bottle soil and water (full on the top) is taken. Finally, the bottle is emptied completely and thoroughly washed, and clean water was filled to the top, and mass (125g)



Fig.4. Separation Al by Organic Solvent and Precipitation of Al.

M_4 is taken. Based on these four readings specific gravity is calculated .Sometimes mixed clay with amount of charcoal gives it porosity**.**

The Scanning Electron Microscopy (SEM): The SEM is a microscope that uses electrons rather than light to form an image. There are many advantages for using the SEM instead of a light microscope. The SEM method provides detailed images of individual grains of clay minerals and Electron Diffraction Spectroscopy (EDS) provides detection of major and minor elements at points on grain surfaces, allowing highly reliable identification from crystal form and composition, as well as direct observation of particle packing and size. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification >3000 times or range. Preparation of the clay samples is relatively easy since most SEM require the sample to be conductive. A few thin sections of clay size fractions coated with an Au-Pd conductor are examined morphologically under (SEM) with link (EDS). The thin sections of representative samples are analyzed for semi-quantitative determination of primary and secondary minerals. Morphologies, as observed by SEM, can also be useful in identification of clay minerals, (Fig. 5a and 5b), (Atkins, 2001; Al-Ani, 2008).

RESULTS AND DISCUSSION

In this study, the results of the experiments and the resultant discussions are given under the following titles: (1) Trace elements (2) Gravimetric analysis (3) Determination of % for Metals Oxides by XRF (4) Calculation of CEC (5) FT-IR spectrum (6) Specific gravity (7) Swelling of bentonite (8) Chemical composition and structural formulate for Bentonite. The results for all measurements are in agreement approximate and reasonable with the standard value of Wyoming USA. The difference between the values may be due to errors because of the instrumental interferences or chemical analysis. Generally, elements present at high concentration can be easier and better determined by XRF, Gravimetric analysis, titration, and AAS methods provide a corpus of well tried methods of maximum accuracy.

Trace Elements: The analyte solution is aspirated into the flame and first is desolated. The resulting aerosol is thermally dissociated leading eventually to ground state atoms. Maximum sensitivity is obtained by using the flame where the atom cloud exhibits the greatest concentration, (Greenland, and Hayes, 1981). To achieve this depend upon the element concerned, the flame stoichiometry and sample matrix. For elements like Cr that tend

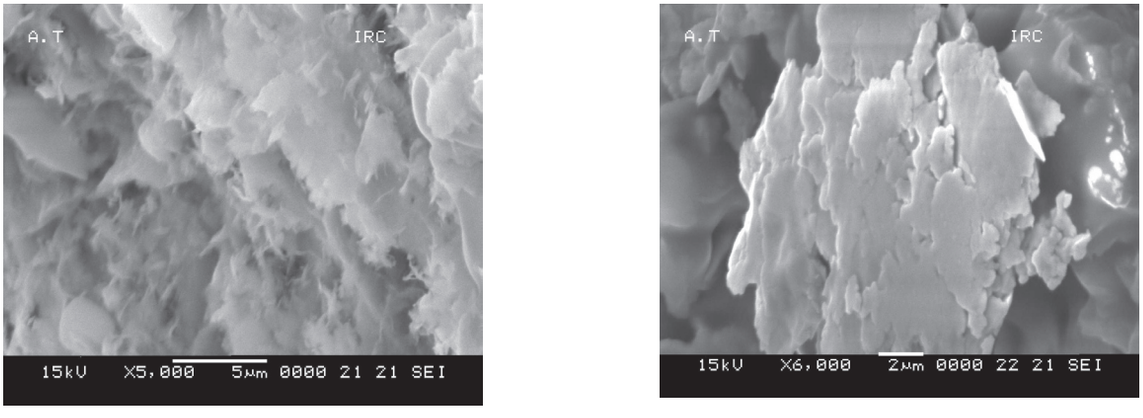


Fig.5. (a) SEM Image before Washing, (b) SEM Image after Washing and drying.

to form very stable oxides, enhanced atomization occurs within a reducing flame. In this experiment is found all trace elements very limited in the sample. The percentage of trace elements (Cd, Cr, Cu, Pb, Fe, and Zn) is found about 0.21% for this clay.

Gravimetric Analysis: Gravimetric Analysis of the clay sample, shows the results in agreement with XRF analysis approximate and reasonable, but it is found different results in measurement, due to errors that may be happened in the instrumental interferences or chemical analysis, also the digestion by HNO_3, the exchangeable cations between the 2:1 layers leave first, and replaced by the H^+ ions. Since only small quantity of (Mg^{+2}, Fe^{+3}, Al^{+3}) leaves 2:1 layer, the change in the $\%M_xO_y$ is small. The mass% of sample MW is determined as follows: SiO_2, 53.75; Al_2O_3, 21.46; Fe_2O_3, 1.4; CaO, 0.97; MgO, 2.13 ; and the results of the same sample by XRF as follows: SiO_2, 54.93; Al_2O_3, 21.46; Fe_2O_3, 1.71; MgO, 3.18 ; CaO, 0.81; Na_2O, 5.48; K_2O, 0.54; TiO_2, 0.3**,** (Table.1).

Determination of % of Metals Oxides by XRF: The most important ability is that of identifying crystalline phases rapidly and simple relatively. Its drawbacks lie in its inability to detect glassy phases and in difficulty sometimes encountered with complex patterns. XRD methods normally cannot give any direct indication of the elemental analysis of the sample. One should especially feed in chemical analytical data, to give the stoichiometry of the system, and optical microscopic finding, to give some indication of presence of glassy phases or of the probable number of separate crystalline phases in the mixture. This method is applicable only to materials with a well defined crystal structure, and hence poorly crystalline or amorphous solids cannot be identified as they don't give clear diffraction patterns. Sample preparation for XRFS is relatively easy, involving direct briquetting of ground samples or various fusion methods, (Willard, *et al* 1988).

Calculation of CEC: The CEC of the sample Murzuq white (MW) that is obtained by leaching process at pH=8 and pH=2 is calculated as follows (Table.1): 84.5 and 20.5 mmoles/kg respectively when leached by 500ppm Ca^{+2}, while CEC increased when leached by 500ppm K^+ at pH=8 as 91.5 mmoles/kg and these values were agreement with the standard value of Wyoming USA (Table. 2). Some exchange capacity for both cations and anions occurs on the edges of silicate clay crystals (Table. 3), whereas the basic cations are principally (Ca^{+2}, Mg^{+2}, K^+, Na^+). Variations in pH cause deviations from equality in the numbers of positive and negative edge charges. AEC increases at low pH=2, and CEC increases at high pH=8 (Table. 4). The likelihood of ionizing significant amounts of (OH^-) depends on the abundance of soil minerals containing (OH^-) and on pH. Relatively untreated clays have a high proportional of 2:1 layer silicate minerals in bentonite. The CEC of this clay is relatively high. Finally, the free (Fe_2O_3) and (Al_2O_3) that accumulate in the clay fraction may cause the AEC to go beyond the decreasing CEC. At pH = 8, practically all the (H^+) in the percolating water is absorbed by the soil irrespective of the salt concentration supplied. At pH =2, the influence of neutral salts increases as the pH falls, resulting in reduce soil acidification and a corresponding increase of the leached acidification. The effects of neutral salts on soil acidification are markedly influenced by the bonding energy (H^+) to the soil

Table (1) Calculation of $\%M_xO_y$ for Metals Oxides

Sample	Al_2O_3%	Fe_2O_3%	CaO%	MgO%	SiO_2%
MW	21.460	1.400	0.970	2.130	53.750

Table (2) Calculation of Concentration for Ca^{+2} by Titration with EDTA 0.01M

Sample	Volume of titrated EDTA for sample, ml	Conc. Ca^{+2} in 500ppm	Volume of titrated EDTA for blank , ml	Conc. Ca^{+2} in blank, ppm	Final Conc. of Ca^{+2} , ppm
MW at pH=2	1.5	120	7.0	560	440
MW at pH=8	5.2	416	1.2	96	320

Table (3) Calculation of K_d and CEC at pH=2 and pH=8 by leached 500ppm Ca^{+2}

Samples	K_d (L/kg)	CEC mmoles/kg
MW at pH=2	2.273	20.5
MW at pH=8	9.375	84.50*

(*) The Standard Values for Wyoming (USA), (Sparks, 2003).

Table (4) Calculation of the Concentration of K^+ from calibration curve at pH=8.

Samples	Conc. of K^+ in 500ppmK^+ at pH=8	Conc. of K^+ in blank at pH=8
MW	425	150

exchange sites. In the majority of situations, the adsorption of anions applied as neutral salts is very small, so that exchange acidity is usually greater than exchange alkalinity. If the soil becomes very acidic then (Al) associated with clay minerals may become soluble in the form (Al^{+3}) or aluminum hydroxyl cation. Soluble aluminum may also be recruited to percolation water through organic substance decomposition. These ions may then become adsorbed even in preference to hydrogen ions, present in soil solution, by the permanent (pH-independent) negative charge in soil clay mineral surfaces. The adsorbed (Al) is in equilibrium with (Al^{+3}) ions in the solution, (Higson, 2005; Harrison, and de Mora, 1996). The solution (Al^{+3}) ions can contribute to soil acidity through their tendency to hydrolyze. In this experiment, it is determined concentration of Ca^{+2} in the samples by titration with EDTA, while concentration of K^+ by flame emission photometer.

Calculation of Final Concentration of Ca^{+2} at pH=8 and pH=2

$$\textbf{Conc. of Ca in ppm} = \frac{(\mathbf{M}\times\mathbf{V})_{\mathbf{EDTA}}\times\mathbf{40}\times\mathbf{1000}}{\mathbf{V_s(ml)}}$$

V= Volume of titrated EDTA, (ml).
M= Molarity of EDTA (0.01M).
$\mathbf{V_S}$ = Volume of sample (5ml)

Calculation of K_d and CEC at pH=2 and pH=8

$$K_d = \frac{(A - B)\times V}{M_S \times B}$$

K_d= Distribution Coefficient (L/kg).
A= Initial Concentration (500) ppm
B=Final Concentration after 24h ppm
V= Volume of solution (50ml).
Ms= Mass of sample (3gm).

…….. (Al-Kateeb, 2001)

$$\mathbf{CEC = K_d \times N}$$

$N = n \times M = 2M = 2\times 0.5/111 = 9.01\times 10^{-3}$ N of $CaCl_2$
$M = N = 0.5/74.5 = 6.71\text{x}10^{-3}$ N of KCl

The distribution of each cation between clay surface and clay solution is controlled by:

1- The charge, size and hydration state of the cation.
2- The density of negative charge on the clay surface, (i.e., the greater of the charge density decrease in diameter of the hydrated cation). The order for group I and II metals cations in increasing charge density is **[$Ba^{+2} < Sr^{+2} < Ca^{+2} < Mg^{+2} < Cs^{+} < Rb^{+} < K^{+} < Na^{+} < Li^{+}$]**.
3- The ionic strength of the clay solution increases because cations are attracted to the anion but anions are repelled.
4- Selective minerals on size criteria may occur or where organic complexion (Humic and fulvic acid).
5- The cations of most common salts can be distributed in the following order according to their adsorption capacity (or energy of their adsorption at clay):

[$Fe^{+3} > Al^{+3} > H^{+} > Ba^{+2} > Ca^{+2} > Mg^{+2} > NH_4^{+} > K^{+} > Na^{+} > Li^{+}$]

Calculation of (SG) for Bentonite in sample MW

$$SG = \frac{[M_2 - M_1]}{[M_4 - M_1] - [M_3 - M_2]}$$

M_1= Weight in (g) of empty dry bottle.
M_2= Weight in (g) of bottle and dry clay.
M_3= Weight in (g) of bottle and dry clay and water required to fill it.
M_4= Weight in (g) of bottle and water required to fill it.

$$SG = \frac{[120 - 80]}{[125 - 80] - [149.60 - 120]} = 2.597 \approx 2.6$$

The IR Spectrum: The FT-IR Spectra in the Figure (1) below show the absorbance of clay samples at a various wave numbers. At 3600-3800 cm^{-1}band, the peaks for both clay samples are the same. The FT-

IR spectra in the Fig. 6 show the absorbance of the clay sample at various wave numbers. The absorption bands of Montmorillonite and Illite is 3635cm^{-1}, 3400cm^{-1}, 1640cm^{-1},1130cm^{-1},1020cm^{-1}, 920cm^{-1}, (Stuart,2004; Hollas, 2004).). Clay minerals may be differentiated by their IR- spectra through study of the bands due to the O-H and Si-O groups. In the O-H stretching region, 3800-3400cm^{-1} for clay minerals, there are 3685 cm^{-1}, 3620 cm^{-1}, 3410cm^{-1} observed. The inner hydroxyl group between the tetrahedral and octahedral sheet in a band near 3620cm^{-1} the other three hydroxyl groups at the octahedral surface form weak hydrogen bonds with oxygen's of the Si-O-Si bonds in the next layer and this result in stretching bands at 3669 cm^{-1}and 3653 cm^{-1}. In the (1300-400cm^{-1}) region, clay minerals show Si-O stretching and bending and O-H bending bands at 908 cm^{-1}, 993 cm^{-1}, 790 cm^{-1} and 748cm^{-1}. For Fig. (1), which mainly have (Al^{+3}) in octahedral position, served well resolved strong band in the 1120- 1000 cm^{-1} region, at 1114 cm^{-1} are observed, and which mainly contains, (Mg^{+2}) in the octahedral sites and (Ti^{+4}) at 747cm^{-1} and 790 cm^{-1} respectively because of the coordination number is (6), the main Si-O band is observed at 993 cm^{-1}. The O-H bending bands are strongly influenced by the layering clays. Where the octahedral sheets are mainly occupied by tetravalent central atoms, the O-H bending band occurs in the 790 cm^{-1} (Table 5). Finally, IR spectroscopy complements XRD methods (Fig. 7).

Table (5) Calculation of K_d and CEC at pH=8 by leached with 500ppm K^+

Samples	Final Conc. in 500ppm K^+	K_d , L/kg	CEC mmoles/kg at pH=8
MW	275	13.64	91.5

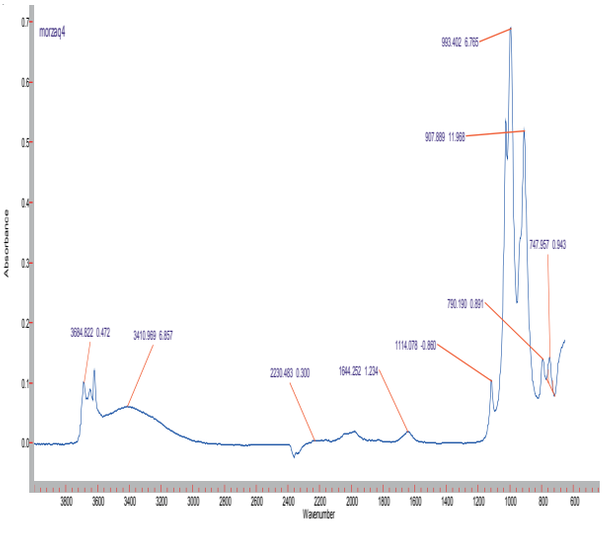


Fig.6. The FT-IR Spectrum of Bentonite Clay for Sample MW

Swelling of Bentonite: When bentonite meets water, it absorbs the water and swells up. This swelling is causes by an interaction between interlayer cations and water molecules. The bonding power between the surface negative charge and interlayer cations of montmorillonite is lower than the interaction energy between the interlayer cations and water molecules. Therefore, the gap between layers is widens as the interlayer cations attract the water molecules (Table. 6). When the interaction between the interlayer cations and water molecules becomes reaches its limit, the swelling stops. Effect of structure properties (ESP), swelling is greatest for Smectite clays that are Na^+ saturated. As the electrolyte concentration decrease, clay swelling increases. As ESP, increases, particularly above 15 times, swelling clay like montmorillonite retain a greater volume of water. Hydraulic conductivity and permeability decrease as ESP increases and salt concentration decreases. Permeability can be maintains if the EC of the percolating water is above a threshold level , which is the concentration of salt in the percolating solution, which causes a 10 to 15% decrease in soil permeability at a particular ESP. If a soil has high quantities of Na^+ and the EC is low, soil permeability, hydraulic conductivity, and the infiltration rate are decrease due to swelling and dispersion of clays and slaking of aggregates.

Chemical Composition and Structural Formulate for Bentonite: The Fig. 7 above, shows the intensities of selected XRD peaks (through 3-70 2θ) characterizing each clay minerals present in the size fraction (e.g. kaolinite 7 Å, Smectite (bentonite) 12 Å and Illite 9 Å) are measured for semi-quantitative estimate of the proportion of clay minerals present

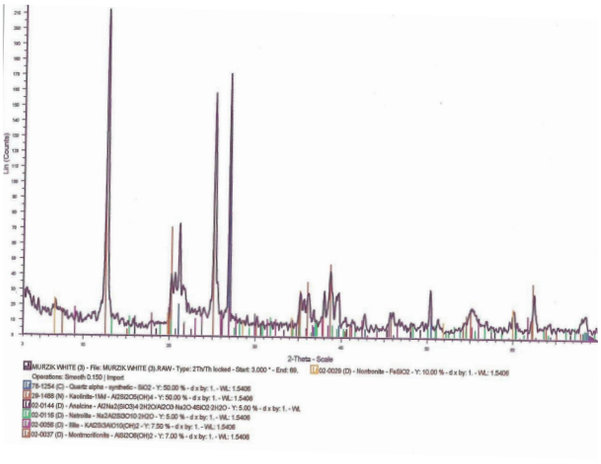


Fig.7. The XRD Analysis of Bentonite Clay for Sample MW

Table (6): Absorption Frequencies (cm^{-1}) for Metal Oxygen Stretching for Tetrahedral and Octahedral Co-ordinations.

Symbols	XO_4		XO_6	
Metal ion(X)	Isolated	Condensed	Isolated	Condensed
Al^{+3}	650-800	700-900	400-450	500-650
Fe^{+3}	550-650	550-750	300-450	400-550
Mg^{+2}	500-550	----------	----------	350-480
Ti^{+4}	650-800	----------	----------	600-650
Zn^{+2}	400-500	400-650	----------	ca. 400

Source: Pantnaik, 2004

in the size fraction < 2µm and 2-16µm. The main peak of 3.30 Å was shifted to 3.10 Å in XRD trace of the sample. Similarly second intensive peak of 14.19 Å was shifted to 14.2 Å. The shifting of other peaks was not significant. The reason for shifting may have been due to the change in crystallographic structure of quartz. XRD trace of quartz supported the results of elemental composition. The mineral related with Fe_2O_3 was not identified in the XRD pattern because it is very small amount and/or amorphous structure. The formula of 2:1 clay is mostly **$[Si_8Al_4O_{20}(OH)_4]$,** whereas:

1. g eq. cations = (Weight % / Atomic weight) × Number of charges of cation
2. There are a total of 44 positive charges and 44 negative charges in a full-cell chemical formula. Then, g eq. cation in total= (g eq. cation×44) / Normalization factor
   Normalization factor = Σ g eq. cation = 5.38
3. Finally, Atoms per unit cell = g eq. cations in total / Valance of cation. (Sparks, 2003). The structural formula of Libyan Bentonite is:

$$[\ K_{0.094}Na_{1.45}Ca_{0.118}(\ Al_{2.92}\ Fe_{0.175}Ti_{0.033}Mg_{0.646})\ ^{VI}(\ Al_{0.52}Si_{7.48}\ )^{IV}O_{20}(OH)_4\ ]$$

This type of clay was called (Na-Montmorillonite) by Wyoming, USA. The Libyan Bentonite was determined by XRD, XRF, FT-IR, and AAS (Table 7) and (Table 8).

CONCLUSIONS

1. During the addition acid at (pH=2) the partial loss of (Mg^{+2}), (Fe^{+3}) and (Al^{+3}) from the 2:1 layers increased the porosity considerably. This probability increases in previous, highly weathered, leached clay because the (Al**)** and **(**Fe) compounds accumulate in such clay, and because most of the ionized (OH^-) combines with (H^+) to form water under acid conditions.
2. Smooth grinding of clay in vibration mill produces change in its physicochemical properties. (a) The grinding for a long time, the crystallinity of the monitored minerals decreases. (b) The intensity of the vibration band in the range 400-1200cm^{-1}in the IR spectrum shows or due to gradual structural changes in the sample MW, (change in the shape and width of the absorption bands are

Table (7): Chemical Composition of Model MW

Oxides	**Molecular weight**	**(Wt. %)**	**g eq. cation**	**g eq. cation in Total**	**Atoms per unit cell**
SiO_2	60.06	54.93	3.658	29.92	7.48
Al_2O_3	101.94	21.46	1.263	10.33	3.44
Fe_2O_3	159.69	1.71	0.06425	0.525	0.175
MgO	40.30	3.18	0.158	1.292	0.646
CaO	56.08	0.81	0.0289	0.236	0.118
Na_2O	61.98	5.48	0.177	1.45	1.45
K_2O	94.20	0.54	0.0115	0.094	0.094
TiO_2	79.90	0.32	0.016	0.131	0.033
Σ % of Trace elements=0.21%			Σ =5.38		

Table (8) Contains of Libyan Bentonite

Materials	% Intensity
Quartz	50%
Kaolinite	50%
Analcine	5%
Natrolite	5%
Illite	7.5%
Nontronite	10%
Montmorillonite	7%
Zircon	120ppm
Trace elements	0.21%

observed, indicating a progressive structural degradation). (c) The reactivity of sample (MW) clay, jointed by CEC, increase during grinding because of increased surface area of clay and porosity.

3. The silicate lattices are not broken down by oxidizing acids, and to give a full break down, and thus to releases fully the associated trace elements, it is necessary to digest such samples in a mixture containing HCl and HF. This breaks the silicate lattices and release the silicon as volatile SiF_4 .With heavily polluted samples it is rarely necessary to use HCl in the digestion as pollutant material does not enter the silicate lattice, and may be extracted with other acids such as HNO_3.

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