

CHEMICAL, PHYSICAL AND MINERALOGICAL, CHARACTERIZATION OF AL-HISHAH DIATOMITE AT SUBKHAT GHUZAYIL AREA, LIBYA

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ABSTRACT

Naturally occurring diatomaceous earth (diatomite) has tested as potential sorbent for several heavy metals and the intrinsic properties were improved by different modification concepts. Where in recent years, contamination of ground and surface water with heavy metals (not biodegradable) and tend to accumulate in the organisms is becoming a major concern. The chemical analyses of the bulk samples are shown as follow were taken from the Subkhat Ghuzyayil deposited in Libya, which is characterized by the expansion and evolution by the late Quaternary age. Silica, alumina and iron oxide were the main constituents of the samples.

The SiO₂ content corresponds to both diatomaceous silica and alumina-silicate minerals present in the samples, Al_2O_3 to alumina-silicate minerals, and Fe_2O_3 to the high amounts of chlorite and vermiculite present in the samples. The CaO and MgO contents are low due to the absence of carbonate minerals. Both are associated with the presence of Ca-smectite, whereas CaO may correspond to the presence of subsidiary Na–Ca feldspars. The loss on ignition (LOI) of the samples is mainly s The Na₂O and K₂O content are mainly attributed to the presence of feldspars and illite.

KEYWORDS: Diatomite Characterization Chemical Analysis, XRD, SEM, XRF for Subkhat Ghuzayil Deposit

INTRODUCTION

The core components of the diatomite valorization are summarized in the chemical and physical properties enhancement that would play a key role as far as uses as industrial rock. Diatomite is white if pure, commonly buff to gray in place, and rarely black. Therefore, under the mineralogy-petrology investigation the main characteristics, features of the diatomaceous earth is the high content of biogenic amorphous silica (opal-A), with form of diatom frustules. The frustules essentially are chemically inert in most liquids and gases. Moreover, the skeletal of diatomite (diatom secretion), microscopically viewed, have quite complex structure with numerous fine microscopic pores, cavities and channels and therefore, well proprietor a large specific surface area and high adsorption capacity.

In addition to the low permeability, high porosity and chemical inertness that will lead to the relation between the pore space and throat size to be useful for modeling the permeability (Enrlich et al 1991b). Combinations of physical and chemical properties of high-grade diatomite make it suitable for many specialized applications, especially for filtration, its principal use. Consequentially, owing to these characteristics, diatomaceous earth can be used as an adhesion of chemical substance onto the surface of the solid (adsorbate), auxiliary material for filtration. The Greeks used diatomite 2,000 year ago as a lightweight building material and in ceramic pottery (Breese, 1994).

On the other hand, it is known that more promising and economically effective in using the valuable mineral

resources for manufacture of adsorbents, filter powders, fillers, and catalysts. In some region, deposits of diatomaceous earth are sufficiently thick and pure to be exploited and processed for certain purposes. Based on the above summary a considerable attention to the chemical and other studies are very attracted to be done.

GEOLOGY OF THE STUDIED DIATOMITE

The known and anticipated diatomite deposits of Al-Hishah Formation in NE of Libya are of marine and lacustrine type (Geoindustria, 1981) which resulted from precipitation of amorphous silica, diatoms secrete siliceous sediment material to form ornate shells (frustules), that have consistent form related to species (spheres and cylinders to discs, ladders, feathers, and needles). Such as these frustules, with their unique and complex shapes, that accumulated as siliceous sediments during Miocene to Pleistocene age (Geoindustria, 1981). The large amount of silica required for growth of diatoms is derived from the nearby expansion and evolution. Preservation of delicate diatom frustules that determine the special technical properties of diatomite requires quiet-water deposition and minimal digenesis (heat, burial, and cementation).

According to the data obtained from the exposed rocks and from excavated locations, two layers of diatomite were found in the upper part of Al-Hishah Formation (Figure 1). The lower diatomite layer with an average thickness of (2 m) exposed in the western part of the study area, and covered by a sequence of clastic layers in the eastern part. The upper diatomite layer with an average thickness of (3m) exposed in the eastern part of the study area, which eroded in the western part.



Figure 1: Schematic 3D View Diagram Showing the Twofold Nature of the Diatomite Unit (Eldernawi, et al. 2013)

MINERALOGY AND CHEMICAL ANALYSES

Optical Mineralogy

A single sample consisted of a large piece of mineral 6-inches by 4- inches by 2-inches thick (Figure 2) sent to test at (M.I.M.R, USA) for petrography study.

This random sample was crushed, pushed through a 200-mesh (75-micron) screen after about 1.7 wt% over size of feed 23 grams material consisted of diatomite, quartz, other white mineral were prepared and examined under a 200-power using a Nikon petrography microscope with polarized lighting (crossed polar).



Figure 2: Sample Sent to Test at (M.I.M.R, 2008 USA)

The crossed polar brighten crystalline minerals and chemicals at many angles of rotation and extinguish the brightness in four rotation regions. However, crystalline minerals and chemicals with cubic symmetry and/or amorphous minerals and chemicals appear dark at all angles of rotation.

Chemical Analyses

Investigations carried out to study mineralogical structure, chemical composition of natural and modified diatomite ore related to Subkhat Ghuzyail deposit utilized chemical analysis using ICP, and X-RF.

A group of 45 samples were analyzed using ICP unit VARIAN –AA 240 FS in P.R.C, Tripoli. All samples were run after complete digestion. The digestion of samples executed by treating .5g of finely ground sample with perchloric acid, nitric acid, and hydrofluoric acid under heating temperature equal to 200°C reduced to 100°C at the end of treatment, with addition of HCl and water. The prepared solution for analyses by ICP represents a concentration of 10g of digested sample per one liter of solution (El-dernawi, et al. 2013).

RESULTS AND DISCUSSIONS

Minerals Identification

Under polarized light microscope photographs (Figure 3 and 4) depict the *Melosira* barrel structures and occasional disk structures with bright crystalline minerals in the background. Photograph (Figure 5) was taken without polarized light. It depicts *Melosira* diatoms and micro-crystalline smectite clay aggregates.



Figure 3: Melosira Barrel, Disk Structures Diatoms



Figure 4: *Melosira* Barrel Structure Diatoms

Based on the visual examination of the material, the sample composition was estimated and Summarized in Table 1.



Figure 5: Melosira Diatoms and Smectite Clay

Table 1: Optical Mineralogical Estimates after (M.I.M.R, 2008 USA)

Mineral Content	Estimated Content
Diatoms (Melosira)	40%
Smectite Clay	56%
Quartz (SiO ₂)	3%
Halite (NaCl)	1%

Chemical Properties

Based upon a review of the data analysis, the material were composed of a significant amount of quartz contaminated with other oxides as impurities. On the other hand practically, diatomite containing less silica and more alumina or even carbonate is being extracted. The results obtained, tabulated providing an overall vision of chemical composition of diatomite samples of the upper layer (Table 2A) and of the lower layer (2B).

El-dernawi et al., (2013) classified the chemical composition into three categories: Major, secondary and minor constituents. Silica (SiO_2) constitutes the major component of the diatomaceous sediments; however the secondary constituents are mainly alumina (Al_2O_3) and iron (Fe_2O_3) . The minor constituents are (CaO), (MgO), (Na₂O), (SO₃).

Sample No.	mple No. $\begin{vmatrix} Al_2O_3 \\ 0_0 \end{vmatrix} = \begin{vmatrix} CaO_3 \\ O_0 \end{vmatrix}$		Fe ₂ O ₃ %	MgO %	Na ₂ O %	SiO ₂ %
LB No.11	1.24	0.58	2.09	0.05	7.74	88.30
LB No.10	0.96	0.37	2.40	0.02	9.59	86.66
LB No.9	1.05	0.12	1.69	0.01	6.52	90.61
LBNo.8	0.72	0.73	1.96	0.03	8.14	88.43
LB No.5	0.78	0.41	1.92	0.11	9.01	87.76
LB No.4	1.19	0.58	1.92	0.15	8.45	87.70
L8c No15	2.42	0.47	4.09	0.16	5.35	87.52
L5cNo.12	0.17	1.48	2.26	0.08	6.30	89.73
L7cNo.13	1.08	0.11	1.83	0.01	6.05	90.91
Average %	1.07		2.24		7.46	88.62

Table 2A: Chemical Percent Values for Samples of the Upper Layer (Eastern Area, Na₂O ≥5.0)

Sample No.	SO ₃ % x 10 ⁻³	L.O.I % x 10 ⁻³
LB No.11		0.026
LB No.10		0.041
LB No.9	0.221	0.026
LBNo.8	0.061	0.021
LB No.5	0.104	
LB No.4		
L8c No15	0.09	0.039
L5cNo.12		
L7cNo.13		
Average%		

Table 2B: Chemical Percent Values for Samples of the Lower Layer (Western Area, Na₂O ≥5.0)

Sample No.	Al ₂ O ₃ %	CaO %	Fe ₂ O ₃ %	MgO %	Na ₂ O %	SiO ₂ %
R5 No.19	1.33	1.91	4.11	0.04	6.12	86.49
R4 No.17	0.42	0.93	0.57	0.18	6.40	97.89
R3 No.16	2.61	0.23	2.11	0.01	5.91	89.13
R3 No.13	0.10	1.47	0.64	0.57	5.09	92.12
R No.8	2.57	0.25	3.78	0.02	5.95	87.43
R No.5	2.29	0.30	3.82	0.03	5.25	88.30
L No.9	2.20	0.24	4.53	0.01	9.63	83.38
LB No.1	0.59	0.86	3.03	0.86	18.34	76.35
L11c No. 21	1.51	1.16	1.76	0.03	7.52	88.00
Average %	1.51	0.82	2.71	0.1	7.79	87.68

Sample No.	SO ₃ % x 10 ⁻²	L.O.I % x 10 ⁻³
R5 No.19	0.03067	0.032
R4 No17	0.01604	0.094
R3 No.16	0.0052	0.017
R3 No.13	0.20514	
R No.8	0.0066	0.024
R No.5	0.0068	0.018
L No.9	0.03352	0.027
LB No.1	0.0165	0.031
L11cNo21	0.04778	0.027
Average %		

The results of the chemical analyses described earlier indicate that the aluminum and iron oxides showing low percentage below the levels given by the Manville (1986, Table 3) and Moler (Mo-clay) which represent the variety found in northwestern Denmark, especially on the islands of Fur and Mors. Calcium oxide and magnesium oxides showed the same behavior like the aluminum and iron oxides. Whereas the lower layer (in the west) showed a little difference in calcium oxide percentages more than that exists in the upper layer (in the east). A remarkable value of sodium oxide

percents distributed as a cluster at NW side of the Subkhat, reflecting a kind of contamination occurred due to their closeness to the shoreline of the Subkhat.

However, the silica percent in all samples are very high reflecting an exceptional percents standing outside the ranges of that given by Moler (cited in Alali, 1991) and Manville (1986, Table 3. An exception was seen in the location of the sample LB No.1 where the silica percent recorded to be around 76.36%.

Components	Lower Layer	Upper Layer	Moler	Manville, 1986	ASTEM St.
Al ₂ O ₃ %	0.1-3.6	0.2-3.2	5.0-7.0	3.8-4.0	
Fe ₂ O ₃ %	0.4-4.6	1.7-4.4	8.0-10.0	1.0-2.0	
Na ₂ O %	1.7-18.4	0.3-9.6		1.0-3.3	Alkaline =2.0 %
SiO ₂ %	76.4-97.9	86.7-94.8	60-80	86-92	85-92
L.O.I %	(1.4-9.4) x 10 ⁻⁵	$(1.7-4.3) \ge 10^{-5}$		0.2-3.6	

 Table 3: Chemical Diatomite Characteristics of Libya Compared with Moler's Standard (Cited in Alali, 1991) and Manville, 1986 Typical, and ASTEM.St

A three dimensional diagrams were plotted to see the distribution of the main oxides $(SiO_2\%, Al_2O_3\%, and Fe_2O_3\%)$ exist in the examined diatom (El-Dernawi et al., 2013). The first diagram (Figure 6A) was plotted to show the distribution of these oxides in the Upper Layer (NE of the study area), while the second diagram (Figure 6B) was plotted to show the distribution in the lower layer (NW off the study area).

The distribution of the selected oxides (SiO₂, Al₂O₃, and Fe₂O₃) spatially in the upper layer showed that the increment in the percentage of concentration of all oxides occur in the middle and upper part of the area. Whereas, the lower part of the area showed that the concentration of SiO₂ less than the upper part, while Al₂O₃ indicates a decrease towards the east opposite the concentration shown by Fe₂O₃ which reveals an increase towards the east. Nevertheless, in the middle of the upper part, both Al₂O₃ and Fe₂O₃ show a decrease in concentration against the distribution of SiO₂.

However, the distribution of the selected $(SiO_2, Al_2O_3, and Fe_2O_3)$ spatially in the lower layer shows less variation than in the upper layer. Concentration of SiO_2 % decrease locally further west of the study area (basin like shape Figure 6B) while Al_2O_3 and Fe_2O_3 show a decrease in concentration in the lower left part of the study area. These variations in oxides distribution are thought to be affected by the supply of materials from the source area to the basin of deposition and due to facies change between marine and lacustrine environments.

Nash (1995), showed that Nevada diatomite characterized by low Na: K and Ca: Mg ratios. Therefore, an attempt was made by testing (18 random samples using XRF) to clarify Libyan diatomite through calculating Na: K and Ca: Mg ratios in both upper and lower layers. The results obtained (Table 4) indicated that the ratios of Na: K were high and that for Ca: Mg were low and high values. The high values of Ca: Mg ratios mainly reflect marine environment. However the high values of Na: K in all samples could be referred to the igneous rocks exist surrounding the basin of deposition, rich in plagioclase feldspar rather than changes in the environment of deposition. The weathered plagioclase is thought to be a major source for Na and Ca concentrations. However, diatomite species indicated that the environment of deposition was not clear marine or lacustrine, but mixed environment of both characterizing the deposition of the upper and lower layers.



Figure 6A: Distribution of Selected Oxides Percent in the Upper Layer (Eastern Part)



Figure 6B: Distribution of Selected Oxides Percent in the Lower Layer (Western Part)

Table 4: Na:K and Ca:Mg Ratios in the Libyan Diatomite Deposits (El-Dernawi et al., 2013)

Sample No.	Na:K	Ca:Mg
Ls	11.28	0.50
L friable	10.11	0.42
Lf	45.44	0.47
L surface	8.94	0.39
D4	11.37	0.50
LM	2.13	0.45
LB1	6.72	0.28
L ca	6.87	0.46
L No.7	5.14	0.43
L 4c	18.28	0.26
R No.5	5.73	0.37
R No.4	5.14	46.74
R No.10	5.57	0.39
R4	2.88	1.85
L11c	16.68	5.29
R5	8.04	1.96
R3	4.73	27.48
LB9	14.87	1.29

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Physical Properties

The diatomite deposits categorized into so called clean, clayey, sandy diatomite types based on their relative abundance of clay, silt and sand. Therefore, four random samples (white, brown) were tested to determine the permeability, porosity using Digital Modular Helium expansion (ratio method) was conducted in the P.R.C of Tripoli. The permeability range obtained was (16.5 to 27.45 md) under L.F.R, H.F.R. with temperature range (22.3°C to 24.8°C), pressure range (66.0 to 20 psi) and flow rate range (70 to 200 ml / min). The four samples tested showed high porosity values as (81.7%, 81.6%, 80.6 and 87.40%), using a correction factor equal to 0.4712.

The skeletal of diatomite, microscopically viewed, has quite complex structure with numerous fine microscopic pores, cavities and channels, therefore they possesses large specific surface area and high adsorption capability (Bentzen, 2008).

Physical properties of the diatomite of Libya were investigated for both, upper layer (Table 5) and lower layer (Table 6). Based on the perforations and open structures in the frustule renders diatomite a considerably lower effective density were results indicated that the bulk density in both layers is ranged between (0.16-0.71) gr/cm³, which infer to considerable range of porosity, that would lead to the use of diatomite in assorted applications and in some areas as excellent reservoir rocks for hydrocarbons. An exceptional high density values were recognized in three places in the lower layer (Table 6). PH values were slightly alkaline in both layers with only two spots in the upper layer showed acidic environment. Porosity was determined by taking into account dry density (Moyle and Dolley, 2003), showed values for the upper layer ranging between (28-42%), while the lower layer porosity ranged between (2-29%). A second way to determine porosity was followed depending on Manville (1983, cited in Anderson, A. R. 1990) in which the whole solid mass was considered to be silicate, the case which orient the value 2.2 as a density of silicate mineral. The second way showed porosity of the upper layer range between (75-91%) while the lower layer porosity ranges from (18 to82%) (Table 5 and 6).

CONCLUSIONS

Fieldwork in Subkhat Ghuzyial diatomite sedimentary deposit (diatomaceous earth) central Libya resulted in the discovery of a thick sedimentary succession that hosts clayey diatomite deposits. The clayey diatomite rock examined is mainly composed of biogenic amorphous silica (diatom frustules) and expanded clays, such as smectite and vermiculite. Silica, mainly amorphous, alumina and iron are the predominant constituents of the raw material studied with low percentage of clay contents.

Estimates of mineral concentration were made using X-RF-determined elemental composition and relative peak heights on the X-RD scan. Mineralogical analyses showed that all samples are mainly composed of Al_2O_3 , Fe_2O_3 , Na_2O_3 , CaO, MgO, SO₃ as impurities with a significant value of SiO₂ (reaching 97%). The high content of SiO₂ raises Libyan diatomite to a high grade row material. The physical properties reflected by this high SiO₂ content reflected good porosity property (reaching 91%), which gives good reason for considering Libyan diatomite as an excellent row material for adsorbent, filters, and medical industry.

The SiO₂ content corresponds to both diatomaceous silica and alumina-silicate minerals present in the samples, Al_2O_3 to alumina- silicate minerals, and Fe₂O₃ to the high amounts of chlorite and vermiculite present in the samples.

The CaO and MgO contents are low due to the absence of carbonate minerals. Both are associated with the presence of Ca-smectite, whereas CaO may correspond to the presence of subsidiary Na–Ca feldspars. The loss on ignition (LOI) of the samples is mainly attributed to loss of the H₂O contained in clay minerals and the SiO₂*nH₂O that is the mineral phase of the diatom frustules. The Na₂O and K₂O content are mainly attributed to the presence of feldspars and illite

The values obtained from calculating Na: K and Ca: Mg ratios in both upper and lower layers, showed high ratio values of Ca: Mg reflecting marine environment, whereas the high ratio values of Na: K referred to the existence of volcanic activity surrounding the basin of deposition rich in plagioclase feldspar.

The variations in oxides distribution is thought to be affected by the supply of materials from the source area to the basin of deposition and due to facies change between marine and lacustrine environments.

 Table 5: Physical Properties of the Diatomite of the Upper Layer (El-Dernawi et al., 2013)

Sample No.	Weight before Calcination	Weight after Calcination	Weight Water M _{eas} (g)	Dry Density	Solid's Volume	Total Volume	Porosity According to Dry Density (%)	Porosity According to sp.gr 2.2(%)	рН	Permeability (cm/s)
LB No. 4	118.02	30.5	87.52	0.2	152.50	240.02	36.46	86.33	6.4	4.09E-05
LB No. 10	190.87	62.02	128.85	0.22	281.91	410.76	31.37	75.82	6.7	3.33E-05
L2C No. 7	195.73	75.37	120.36	0.25	301.48	421.84	28.53		7.0	2.04E-05
L10C No.19	349.35	61.95	287.4	0.16	387.19	674.59	42.60	91.10	7	6.50E-05

*Special description of the title. (Dispensable)

Table 6: Physical Properties of the Diatomite of the Lower Layer (El-Dernawi et al., 2013)

Sample No.	Weight before Calcination	Weight after Calcination	Weight Water M _{eas} (g)	Dry Density	Solid's Volume	Total Volume	Porosity According to Dry Density (%)	Porosity According to sp.gr 2.2(%)	рН	Permeability (cm/s)
R No. 3	148.08	47.48	100.6	0.2	237.4	338	29.76	82.34	7.1	1.97E-05
R No. 1	159.42	54.37	105.05	0.22	247.14	352.19	29.83	80.95	7.8	1.87E-05
R No. 18	436.03	285.14	150.89	0.71	401.61	552.50	27.31	53.79	7.2	2.98E-06
R4 No. 17	437.9	267.96	169.94	0.62	432.19	602.13	28.22	58.25	7.7	6.52E-07
R5 No. 19	194.68	74.08	120.6	0.22	336.73	457.33	26.37	78.17	7.3	1.06E-05
R2 No. 11	236.5	213.82	22.68	0.23	929.65	952.33	2.38	18.92	7.2	3.88E-06
R3 No. 13	305.45	189.69	115.76	0.62	305.95	421.71	27.45	57.31	8	5.74E-06

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