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SEDIMENTOLOGICAL AND TECHNICAL STUDIES ON THE MONTMORILLONITIC CLAYS OF ABU TARTUR PLATEAU, WESTERN DESERT, EGYPT

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One of the most known sedimentary formation among Egyptian Upper Cretacous rock units is named Duwi Formation (Lower Maastrichtian), an outcrop at the Abu Tartur plateau, Kharga Oasis, Western Desert, Egypt. This formation displays three montmorillonitic clayey layers. The investigations of these sediments provide information on the texture, constituents and type of clay minerals, which helps define and describe their physical and technical properties.

Granulometrically, the selected samples have siltstone, mudstone and claystone facies. Mineralogical analysis of the studied deposits proved that the clay minerals compose mainly of montmorillonite, in addition to small amount of glauconite, and traces of illite. Scanning electron microscopy revealed three main micro-structures, namely honeycomb, matrix, and turbulent.

Acid activation of eight samples was performed using hydrochloric acid. The efficiency of activation was examined by measuring their bleaching capacity to crude cotton seed oil, and changes in their surface areas. The acid treatment resulted in more than 4-fold increase in the activity of the pretreated bentonite samples. The extent of activation was found to be pronounced after the first 30 minutes of acid treatment.

Key words: clays, montmorillonite, acid activation, bleaching ability, drilling mud, Abu Tartur

INTRODUCION

The studied samples have been collected nearby the Abu Tartur mine, which is located at the intersection of longitude 30º E. and latitude 25º30´N. This area had attracted the attention of many researchers since the discovery of great phosphatic deposits in 1967 and is still under focus due to its strategic position as a source of raw

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materials, especially the phosphates, clays and other rocks. Several lithologic, biostratigraphic, hydrological, geotechnical, and technological studies were carried out either on surface outcrop or subsurface. They were mentioned by Said (1990) and Sediek (1999).

Recently, the Kharga or New Valley government have new thoughts for encouraging scientists to carry out applied or technical studies on the exposed rocks to facilitate exploitation of claystone and mudstone as raw material for industry of ceramics, bricks and others industrial purposes. The most recent studies in this field were described by Sediek and Amer (2001) and Sediek (2005).

Bleaching and adsorption properties of bentonites towards oil and dyes are normally increased by acid treatment (Russu et al., 1979). Acid treatment of clay leads to removal of some ions from their frame structure, which cause an increase in their surface areas. However, caution should be taken during acid treatment of montmorillonite to avoid the formation of non-active hydrated silica. The efficiency of activation process of montmorillonite depends mainly on the nature of acid, its concentration, temperature of activation, and the nature of clay itself , especially the Al_2O_3: SiO_2 ratio. The aim of the present work is the activation of montmorillonitic clays of Duwi Formation exposed at Abu Tartur plateau deposits to sustain its suitability to be used in drilling mud.

MATERIAL AND METHODS

Ten representative samples of surface exposed sediments on the Abu Tartur Plateau, Kharga Oasis were collected from the Duwi Formation. These samples have been exposed to megascopic investigation. Carbonate content, insoluble residue and organic matter content had been determined in the ten fine grained argillaceous samples. These samples were mechanically analyzed by wet method according to their grain-size following Carver (1971). The obtained data were illustrated in Table 1 and on a sand-silt-clay triangle (Braja, 1990) in Fig. 1.

The selected clayey samples were examined by X-Ray Diffraction (XRD) in Moscow State University using Dron 3-model instrument with CuK radiation. The resulted XRD diffractograms were interpreted using Krotova and Kazakova (1984) and Starkey et al. (1984) flow sheet to define the clay mineral type of these samples. The same samples were investigated by scanning electron microscope (SEM). These investigations were carried out at both Moscow State University and Alexandria University, Faculty of Science, Central Laboratory.

Acid activation was performed by treating these clayey samples with HCl having different concentrations between 1 and 6 M. The clay ratio was kept at 1:2.6. Treatment was carried out at 95ºC and different leaching periods varying from 20 minutes up to 8 hours. A two-gram montmorillonite clay sample was added to 5 cm^3 of HCl in three–neck flask fitted with a thermometer, reflux condenser, and stirrer. A 0.25 g of the treated bentonite was added to 20 cm^3 of crude cotton seed oil in a wide test tube immersed in an oil bath kept at 100º C for 30 min with stirring. The optical density of the bleached oil was measured by a Unicom Spectrophotometer SP 500 at 460 nm. The total surface area of activated solid products were determined using the ethylene glycol mono ethyl ether (EGME) method.

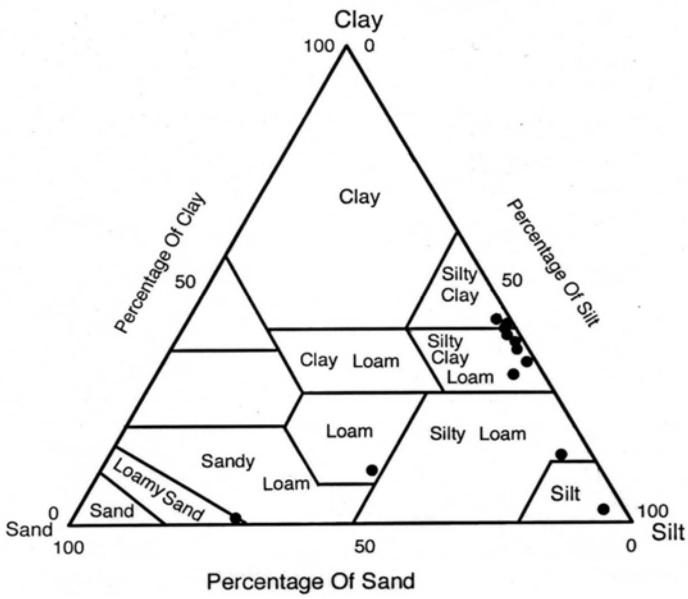

Fig. 1. Textural classification of the studied sediments (after U.S. Department of agriculture classification, Braja, 1990)

SEDIMENTOLOGICAL CHARACTERISTICS

GRANULOMETRIC INVESTIGATION

The studied fine sediments have subjected to granulometric analysis using the pipette or wet method. The obtained data are illustrated in Table 1. According to Shepard (1954) classification of fine-grained sediments, the Duwi Formation Sediments (DFS) lie in clayey siltstone, siltstone, silty mudstone and claystone in a decreasing order of abundance. It means that the common facies among these sediments is the siltstone, while the majority are represented by clayey siltstone and pure siltstone. The siltstones of Duwi Formation tend to be clayey in nature.

The granulometric analysis data revealed two main categories of rocks. The first and more common is the siltstone and the second is the mudstone and claystone. The investigated siltstones have clayey nature, occasionally exhibit glauconitic, phosphatic contents or even ferruginated tint. The first two materials were observed frequently in the DFS. Compositionally, the siltstone have a calcareous character, where the carbonate content ranges from 11.88 to 41.42 % in the DFS. Granulometrically, the siltstones include three subfacies, namely pure siltstone, clayey siltstone, and sandy siltstone. The second subfacies is the most frequent one. In the case of mudstone and claystone, these rocks display the mentioned megascopic characters as in siltstones. According to the frequency distribution of clay fraction among the studied sediments, these facies are low in abundance (Table 1 and Fig.1).

The obtained data of the analyzed sediments were plotted on the triangle of textural classification of sediments (Braja, 1990). It had appeared that the samples fall into several zones (Fig. 1). The DFS samples lie in Silt, Silty loam, Silty clayey loam, and Loam.

Table 1. Granulometric analysis of the representative montmorillonitic sediments of Abu Tartur Plateau

Clastic constituents	Sample No.						
	Du. 27	Du. 26	Du. 25	Du. 23	Du. 21	Du. 17	Du. 16
Sand	0.84	0.38	0.08	0.40	0.76	12.52	3.39
Silt	58.21	60.21	50.78	58.49	60.32	71.14	82.63
Clay	40.95	39.40	49.12	42.05	38.92	16.34	13.43

MINERALOGICAL INVESTIGATION

The purpose of the present part is to describe the distribution and characteristics of mineral composition, especially the clay minerals of the fine sediments, and evaluate the clay mineral data in terms of environmental conditions and its effect on the technical properties. Six samples were analyzed using the X-Ray diffraction method. These samples were selected as good representative and cover the collected fine-grained sediments, which seem to be rich in montmorillonite clay mineral.

X-RAY ANALYSIS OF BULK SAMPLES

X-ray diffractogram of the investigated samples revealed the presence of two main mineral types, that is clayey and non-clayey. The detected clay minerals include smectite, illite, kaolinite, glauconite, while the non-clay minerals include quartz, feldspar, carbonate minerals (calcite and dolomite), evaporite (anhydrite or gypsum) and others as jarosite, pyrite and apatite. Analyzing the obtained data, two mineral associations were recognized. The first association includes high smectite (40 - 91 %), quartz (8.80 - 30.8 %), as well as traces of illite and kaolinite. The second association includes high glauconite (15.40 - 88.10 %), quartz (3.10 - 35 %), and traces of illite.

X –RAY ANALYSIS OF CLAY FRACTION

Ten samples of separated clay fraction were selected and investigated by the X-ray analysis. Three of them are illustrated in Fig. 2. Three runs of oriented clay particles (air dried untreated glycolated and heated to 550 ºC) were carried out. The X-ray diffractograms of two selected samples of Duwi Formation (Du.27, 23) show a uniformity in their recorded peaks and consequently refer to similar clay minerals, where the air dried untreated runs have 1.421 nm, this peak was expanded to 1.78 nm. By heating, this peak collapses to 1.0 nm with the appearance of weak 0.5 nm peak indicating montmorillonite clay mineral. The diffractogram of the third sample (Du.22) shows more or less different positions of the peaks, where the air dried untreated run shows 1.45 nm. Under glycolation this peak shifts to larger spacing 1.8 nm with increasing in its intensity and by heating this peak shifts to smaller spacing of 1.0 nm, indicating randomly interstratified smectite–chlorite. This diffractogram also shows 0.716 nm peak under air dried run, and remained at the same spacing through glycolation run, while destroyed during heated run, indicating kaolinite of disordered type.

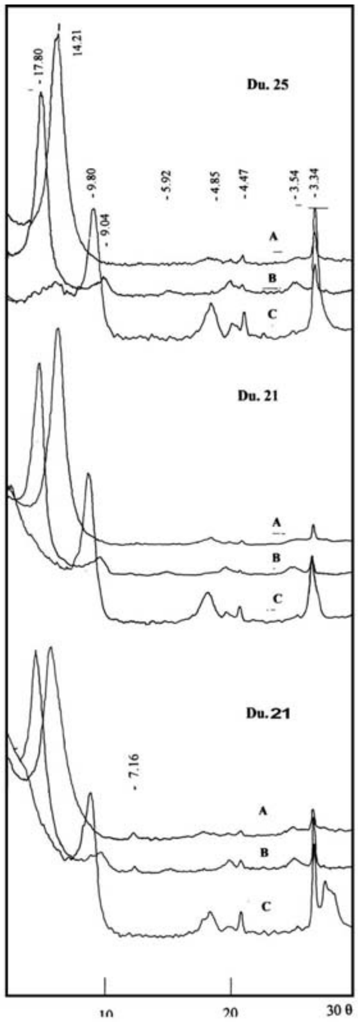

Fig. 2. Diffractogram of the representative clay fraction of the Upper Cretaceous sediments of Abu Tartur Plateau
A: Oriented air dried run,
B: Glycolated slide run,
C: Heated slide run

Table 2. Mineralogical analysis of the representative montmorillonitic sediments of Abu Tartur Plateau

Sample No	Clay Minerals				Non-clay Minerals					
	Sm.	Illite	Ka	Gl	Q	F	D+C	An+G	J	O. M
Duwi Formation Sediments										
Du. 27	91.00	0.10	0.10		8.80					
Du. 26	61.50	0.70	1.10		30.80	5.90				
Du. 25				50.90	22.80			7.89	16.00	
Du. 23	89.10				9.20	1.60				
Du. 21	83.20		3.20		8.20	1.25	2.40			
Du. 17	73.40		0.60		17.30	2.60			3.80	P= 1.2
Du. 16				88.10	3.10			0.01	7.50	P=1.7
Du. 15	40.00	30.00			30.00					

Sm = smectite, Ka = kaolinite, Gl = glauconite, Ki = palygorskite, Q = quartz, F = feldspar, D = dolomite, C = calcite, An = anhydrite, G = gypsum, J = jarosite, P = pyrite, A = apatite, O. m = other minerals

MICRO-TEXTURES AND NANO-STRUCTURES

Depending on mineral composition, shape and degree of dispersion of primary clay particles as well as sedimentation conditions, micro-aggregates in clayey sediments may take different forms and may range in diameter from fractions to score of micrometers (Grabowska-Olszewska et al., 1984). The studied samples show broad ranges of form and size, they vary from sheet-like micro-aggregates and micro-blocks formed by illite (Figs. 3 b-e) and montmorillonite (Fig. 4a-c), occasionally show isometric forms.

The type of contacts of micro-grain or micro-crystal are face-to-edge or edge-to-edge (Fig. 3a) and face-to-face (parallel platelets) as in Fig. 3e.

The obtained microphotographs show a wide variation of sedimentary nano-structures, the first and most common microstructure is the honey comb microstructure. It is characterized by the presence of open nearly isometric cells 2-5 μm in size and the cells wall are mostly montmorillonite–illite (Fig. 3a,b). This structure is considered as a universal feature of marine sediments. Such structure reflects a certain conditions of formation, which express the difference in mineral composition (montmorillonite, illite, occasionally chlorite), temperature regime and salinity in their basin of sedimentation. A characteristic feature of honey comb microstructure in marine sediments is the presence of a great amount of organic residues (Grabowska-Olszewska et al., 1984).

The second microstructure is the matrix type, which is characterized by the presence of a continuous nanoriented clay mass (matrix), that contains irregularly arranged inclusions of silt (Fig. 3c). This microstructure indicates illite and mixed layer composition. It is most probably formed from reconstruction of the honey comb microstructure during compaction process (Grabowska-Olszewska et al., 1984).

The third recorded microstructure is the turbulent type (Fig. 3d,e) in which the orientation of clay material results in a pronounced anisotropy of physical and mechanical effects. This microstructure most probably occurred during compaction of clayey sediments containing both structure honey comb and matrix microstructures. The turbulent microstructures commonly occur in marine environment with medium degree of compaction.

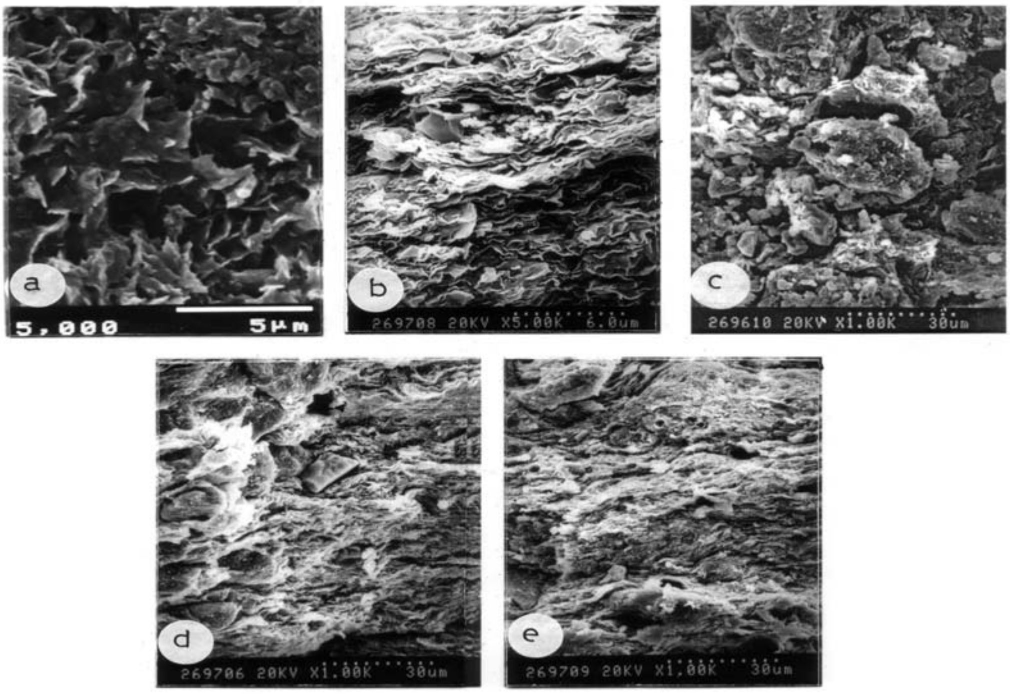

Fig. 3. Scanning Electron Microscope microphotographs of representative clayey sediments
a, b: hony comb microstructure with montmorillonite and illite cell walls, c: Matrix microstructure with illite and mixed composition, d, e: turbulent microstructure type

According to the mutual grain-to-grain relationship, two main types of micropores were defined: inter-granular and intra-granular micropores. The first type is illustrated in Fig. 3a-e, which resulted in clayey sediments with silty grains. The second type is most probably due to diagenetic dissolution or leaching process (Fig. 3d), the pore here takes more or less an isometric form with several microns in diameter (≈ 4μm).

In reference to the Grabowska-Olszewska et al. (1984) classification, the recorded pores divided into two main types: ultrapore (< 0.1 μm in size), which are completely filled with absorbed water and micropore (0.1-10 μm), in which capillary rise as well as filtration under gradient take place. The first type is not easy to observe, while the second one could be observed with isometric morphologic form (Fig. 3a-c).

ACTIVATION OF ABU TARTUR CLAYS

The montmorillonite type clays are usually subjected to some treatment in order to improve definite properties which make it suitable for the purposes of which the montmorillonite is required for. Some of these treatments include alkali activation, acid activation and thermal treatment which are of great importance in the industrial uses (Ross, 1964). Preliminary acid activation test were carried out on the investigated samples of Abu Tartur clays.

BLEACHING ABILITY

Acid activation was performed using HCl as an activation agent with different concentrations (1, 2, 4, and 6 M), at constant clay/acid ratio of 1:2.6 and constant temperature of 95º C for leaching period of 20 min - 10 hours. The activation extent was determined by measuring the external surface area of the activated samples using BET method. Furthermore, the bleaching was carried out on cotton seed oil using a clay oil ratio of 1:80 (g/cm^3) at 100ºC for 30 minutes.

Table 3. Bleaching ability of montmorillonitic clay samples of Abu Tartur Plateau

Sample No.	Leaching periods, min					
	Untreated	60	120	180	300	480
Du. 27	53.6	93.7	92.4	96.9	98.9	94.4
Du. 26	43.7	89.6	92.4	96.1	94.1	93.2
Du. 25	51.1	90.0	90.4	96.0	96.0	--
Du. 23	53.2	90.6	91.5	96.3	92.3	--
Du. 21	50.4	91.1	91.7	98.9	95.9	--
Du. 17	48.4	91.5	89.2	91.9	91.3	--
Du. 16	39.6	89.4	92.3	96.9	96.2	--
Du. 15	46.9	87.5	89.9	93.9	93.9	--

It was found that the bleaching ability and the external surface area of the acid treated samples were rapidly increased after the elapse of the first 20 minutes. They acquired limited values were of 3.5-fold and 5-fold respectively higher than those of the untreated sample. This may be attributed to the great ease with which a new active compound is formed as a result of the high reaction rate between smectite and hydrochloric acid. At leaching period longer than 20 minutes, a slight decrease in the bleaching ability was observed as a result of the complete destruction and collapse of smectite structure. At prolonged leaching periods, the bleaching ability was slightly increased due to the slow response of the clay minerals (e.g. kaolinite) to the action of hydrochloric acid. It is noticed that the bleaching ability does not appreciably increased while the concentration of acid increase, where values of 85-100% were obtained at acid concentration range of 1-6 M respectively. Under the optimum leaching conditions, only 0.94g of the activated clays (using 6 M HCl) develop the same bleaching efficiency effect of 1 g of the standard bleaching material. The same effect is only remarked with 5.4 g of the unactivated samples.

SURFACE AREA

Changes in the total surface area of the studied montmorillonitic clay samples, as well as their respective activated products treated at 95º C with 6M HCl for different periods ranging from 1-5 hours. The results are shown in Table 4.

Table 4. Surface areas of montmorillonitic clay samples of Abu Tartur plateau

L.P./hours	Surface area (m^2/g)							
	Du. 15	Du. 16	Du. 17	Du. 21	Du. 23	Du. 25	Du. 26	Du. 27
Untreated	19.0	37.7	26.1	32.4	24.3	26.7	32.0	32.7
1	123	122	140	130	174	173	115	116
3	155	144	148	105	130	128	128	192
5	111	133	196	162	158	172	148	210

The obtained results in this Table illustrate that the starting surface areas are considerably different from one sample to another ranging from 19 to 37.7 m^2/g. This may be attributed to the changes in the nature of the oxide components which are present in each sample, as well as its position as exposed sample or taken from the inside Abu Tartur mine. A sudden increase in the surface area was noticed after a short period of acid treatment (during the first hour), the increase ranges from 5 to 7-folds. There was a further gradual increase in the surface area with further acid treatment. A slight increase of the total surface area followed by a gradual decrease was observed upon increasing the leaching period. This increase is related to the destruction of the smectite structure. The sharp increase in the surface area could be interpreted due the dissolution of soluble salts, carbonates and some free oxides that lead to the creation of new space and pores accessible to adsorption, while the slight decrease of surface area, that happened after 3 hours, in some cases may be due slight collapse in the clayey flakes.

It can be noticed that the total surface area of the studied samples range from 115-210 m^2/g indicating the presence of high internal surface area values which are mainly due to the presence of smectite minerals. Comparing the total surface areas obtained from the studied samples with those of pure montmorillonite (250m^2/g) and kaolinite (70m^2/g). It can be estimated that the studied clays contains a considerable amount of smectite minerals.

GEL INDEX

Determination of the gel index was carried out where 4.2 g clay, 7-8 g alumina and 0.6 g magnesium oxide were mixed with 100 cm^3 of distilled water for 60 minute in a measuring cylinder. The mixture was allowed to stand for 24 hours and the volume of the suspension liquid is measured and subtracted from 100 cm^3. This gives the value of gel index in percent. For comparison between the obtained values of yield test and gel index, it is clear that the activated Abu Tartur montmorillonite are of relatively high yield values (39 barrel/Mg). The plastic viscosity is relatively high (7 cP) and indicates that the studied samples can be used in preparation of drilling fluids for petroleum industry.

CONCLUSIONS

From the aforementioned studies, it is concluded that the fine-grained sediments of Upper Cretaceous of Abu Tartur Plateau are poorly fossiliferous and vary in color from gray, green to black in Duwi Formation sediments (abundance of black shale). According to the technical textural classification, the studied sediments lie in five zones, ordered according to their increasing in abundance, loam, silt, clay, silty clay, and silty clay loam. Based on the quantitative and qualitative estimation of mineral composition through the study of the X-ray diffractograms, two main mineral association were recognized: high smectite-quartz-traces of illite and kaolinite, high gluaconite-quartz-trace of illite. Furthermore, the clay mineral has good crystallinity (high, intense peaks). With reference to the micro-texture and microstructure, three main micro-structures were defined namely, honey comb, matrix, and turbulent micro-structure, which refer to a vary paleo-condition of deposition. Experimentally, it has been noticed that the most effective condition of the bleaching efficiency of the studied samples were activation with 6 M HCl at 95 ºC, and using clay to acid ratio (1 g : 2.5 ml) for 5 hours. The surface area of the studied montmorellonitic clay samples increased after short period of acid treatment (one hour) and the increase ranged between 5 to 7-folds. Displaying the main granulometric, mineralogical composition, nanostructure and other physical parameters after acid activation, shows that the studied Abu Tartur clays can be used in preparation of the drilling mud.

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Jednym z najbardziej znanych utworów osadowych skał Egipskiego Górnego Cretacous jest formacja Duwi w Dolnym Maastrichtianie wysadu Równiny Abu Tartur Oazy Charga na Egipskiej Pustyni Zachodniej. Formacja ta posiada trzy warstwy montmorylonitowe. Badania osadów dostarczyły informacji o teksturze, składnikach i typie minerałów gliniastych, co pomaga definiować i opisywać ich fizyczne oraz techniczne właściwości.

Badane próbki zawierały facje pyłowe, mułowe i gliniaste. Analiza mineralogiczna badanych osadów wykazała że minerały gliniaste zawierały głównie montmorylonit, a także małe ilości glaukonitu i ślady illitu. Skaningowa mikroskopia elektronowa wykazała trzy główne mikro-struktury, a mianowicie plastra miodu, matrycową i chaotyczną.

Przeprowadzono aktywację kwasową ośmiu próbek stosując kwas chlorowodorowy. Skuteczność aktywacji badano poprzez pomiar zdolności do wybielania surowego oleju z nasion bawełny oraz zmiany w ich obszarach powierzchniowych. Aktywacja kwasem prowadziła do czterokrotnego wzrostu aktywności próbek. Stopień aktywacji był znaczący po pierwszych 30 minut traktowania kwasem.