

Towards A More Safe Environment: (2) Characterization of Some Clay Sediments in Egypt for Safe Environmental Applications

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Abstract: Due to the increase concerns about the environmental pollution problems, it is so important in waste management to perform an accurate exploration of geological barriers, which are suitable for waste materials disposal. Clay sediments play an important role as natural adsorbents to immobilize different types of contaminants (heavy metals, organic pollutants and nuclear elements) from ecosystem. In the present study three natural clay sediments differ in their mineralogical composition were selected. The clay samples were collected from either clay exploitation localities or from nearby radioactive mineralization in Egypt. The clay samples (kalabsha, Abu-Tartur and El-Hafafit) firstly investigated radiometrically by measuring some radioactive elements by Gamma-ray spectrometry. Then physical , mechanical and chemical characteristics were recognized. The mineralogical composition of selected clay sediments was characterized by the XRD analysis, IR spectroscopy and DTA techniques. Analyses of the major and trace elements were carried out as indication of chemical composition of the sediments. Obtained results indicated that the sediments are safe and free from any radioactive materials or toxic metals and had suitable cation and anion capacity, low salinity; clayey fraction, dominated by clay minerals with high percentage. Thus, these sediments considered excellent geological barriers and suitable for several environmental applications.

Key words: Clay sediments, DTA, Ecosystem, IR, Safe environmental applications, XRD, XRF

INTRODUCTION

From the geological point of view, geological barriers should confine layers of adequate thickness, which is the case in clayey sediments. In addition, one of the most critical parameters concerning the safety and the long-term working of the landfill construction is the capacity of adsorption and permeability.

In fact, these sediments represent excellent natural barriers due to their small grain size, their specific surface area and their diagenetic processes (which cause a high natural density). Besides, their ability to close fissures and cracks (which may form paths for leachates). In addition, their chemical reactivity permits them to immobilize important contaminants from the ecosystem, barnett *et al.* (2000), Abdallah (2000), Gadelle *et al.* (2001), seaman *et al.* (2001), Abdallah *et al.* (2005), Abdallah (2006) potgieter *et al.* (2006), Malandrino *et al.* (2006), julide and resat (2006) and Ridvan say (2006).

In this context, it is worthy to mention that the clayey sediments and natural clay minerals contain different percentages of other reactive components such as Fe - Mn oxides and hydroxides besides carbonates and organic matter that fix heavy metals and other pollutants. For all these reasons, clayey sediments and clay minerals are qualified as natural barriers. However, alteration of clays due to interactions with leachates should be considered.

The aim of this study is to characterize some sediments in Egypt before utilization as safe barriers in several environmental applications i.e. removal of heavy metals and other pollutants from wastewater, safe disposal of waste radioactive materials, save nuclear material from lost and loaded the sediments by nutrients to use as a conditioner to increase the fertility of new reclaimed poor soils.

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MATERIALS AND METHODS

Clay Sediments Location:

Three natural clay sediments differ in their mineralogical composition were selected. The samples were collected from either the exploitation localities or from nearby radioactive occurrences in Egypt Fig. (1). these sediments include:

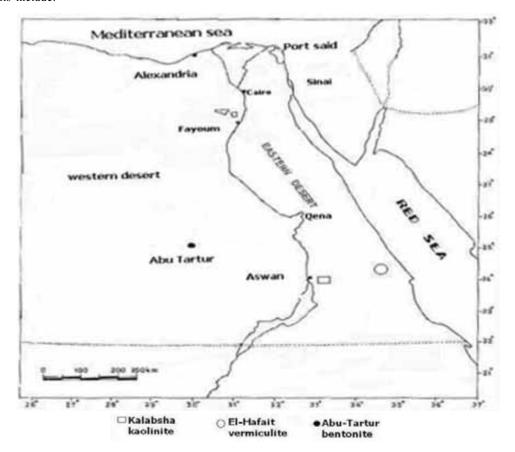


Fig. 1: Location map of studied clay sediments.

Kalabsha Sediments (Aswan):

Kalabsha area lies between longitudes 32° 00' and 32° 30' E and latitudes 23° 00' and 23° 45' N.

Abu- Tartur Sediments (Western Desert):

Abu-Tartur plateau lies between longitudes 25° 00' and 26° 00' E and latitudes 29° 00' and 30° 30' N.

El Hafafit Sediments (Eastern Desert):

El Hafafit area lies between longitudes 34° 20′ and 34° 50′ E and latitudes 24° 20′ and 24° 50′ N.

The collected samples were grinded in a porcelain ball mill, washed with distilled water to remove soluble impurities and wet sieved through 350 mesh sieve (45 μ m), homogenized and < 45 μ m fraction was collected.

Methods:

Radiometric Analysis:

The radioactive elements; U, Th, Ra and K are measured radio-metrically by gamma- ray spectrometry multichannle analyzer. This system consists of NaI (TI) Bicron scintillation detector, 76x 76mm connected with an amplifier model NE-4658 and a high voltage power supply, model Tc-592 with HV digital display. In this technique, four energy regions of interest representing Th-234, Pb-212, Pb-214 and K-40 isotopes are used to

estimate U, Th, Ra and K, respectively. Uranium and thorium are measured indirectly using their corresponding gamma-ray emitting daughters, Th-234 and Pb-212 (Matolin,1991). Consequently, uranium is expressed as eU (equivalent uranium) and thorium is expressed as eTh (equivalent thorium). The probable measurement error is generally $\pm 10\%$.

The rock samples are crushed well (to grain size 1mm) and a proper weight (350-400 gm) of each sample is mixed well to avoid the non-homogenous distribution of minerals and then placed in standard size plastic container. The rock sample sealed well and stored for at least 21 days where radon is back to the normal state and attains radioactive equilibrium. The measurement is carried out through three main steps; energy calibration, sensitivity calibration and gamma ray assaying. The energy calibration is carried out by two radioactive calibration sources, Cs-137 and Co-57 whereas; the sensitivity calibration is achieved using four artificial standard sources (geological reference materials) including NMA-U, IAEA-Ra, IAEA-Th and IAEA-K. The gamma ray assaying includes determination of the background count rates, measurement the gross counts of U, Th, Ra and K in the concerned samples for 1000sc. These data as well as the sample weight are introduced in a computer program (analysis) to obtain the concentration of the radioactive elements (eU, eTh and eR in ppm and K in %) in the rock sample.

Chemical and Mechanical Characteristics:

According to Black et al. (1985), the different analyses carried out as follows:

Mechanical analysis by pipette method, cation exchange capacity (CEC) by sodium saturation method, While pH and electrical conductivity (EC) were determined by glass electrode and electrical conductivity device, respectively. anion exchange capacity (AEC) by Wilson (1994).

X-ray diffraction analyses (XRD):

Thin slurry of the separated clays deposited on a glass slide, air dried at room temperature and subjected to X- ray diffraction analysis. In the present study, a Philips X-ray unit (PW 3710) with a generator model PW 1830 fitted with a scintillation counter model PW 3020 was used. The X-ray tube used was a Cu target model PW 22 33 attached with a Ni-filter. The tube operated at 40 kV and 20 mA. The XRD analysis carried out on their clay fractions (< 2 microns). The identification of the clay minerals achieved through the X-ray diffraction pattern using the American Standards and Testing Materials (ASTM) Cards, Index to X-ray Powder Data Files.

Infrared Spectroscopic Analysis (IR):

Infra red absorption spectra in the region of 400 cm⁻¹ to 4000 cm⁻¹ were recorded using KBr sample pellets. The samples were prepared as pellet method according to Russell and Fraser (1994). In the present work, A Bruker Vector spectrophotometer model FT-IR-22, Germany in the region of 4000-400 cm⁻¹ used.

Differential Thermal Analysis (DTA):

The studied clay samples have been thermally analyzed using a Schimadzu DT30 instrument. The latter is characterized by a recording vacuum, thermo-analyzer with a high temperature (1100°C) microplatinum heater (furnace). The working conditions adopted in the present analysis were adjusted as follows:

- *Heating Rate: 20°C/min. in a standing air.
- *Sensitivity: \pm 50 μ V.
- *Chart Speed: 5 mm/min.

Chemical Analyses:

Analysis of the Major Oxides:

Due to wide variations in the composition of the clayey sediments, a complete chemical analysis of these samples was accomplished. The rapid silicate, carbonate and phosphate analysis method of Shapiro and Brannock (1962) used in this study. This method involves the preparation of two main solutions, namely an alkaline solution for SiO₂ determination and an acid solution for the determination of most of the other oxides like Al₂O₃, CaO, total iron, Na₂O, K₂O, etc. Special sample portions used for the determination of the anions CO3⁻ HCO₃ SO₄ and Cl⁻ Proper ignition loss at various temperatures was also determined. A schematic diagram illustrated in Fig. (2) showing the main analytical routed of this method.

Analysis of Trace Elements:

A number of trace elements in the clay samples were achieved by X-ray fluorescence (XRF) using a Philips PW X-UNIQUE II X-ray spectrometer together with a Mo-target tube operated at 50 Kv and 30 mA. A series of natural standard clay samples were used for quantitative determination. A LiF 200 analyzing crystal

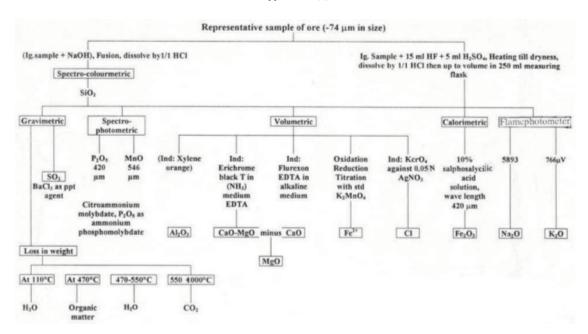


Fig. 2: Schematic diagram shows the route of the used analytical methods for the determination of the major oxides.

(2 d = 4.028 A°) and a flow proportional counter together with a scintillation counter for detection used. Pulse height analysis with the lowest permissible base lines and channel width used to avoid interference. A 2-gram portion of each powdered sample pressed into pellets using aluminum cups. Analyzed trace elements include Ba, Cu, Nb, Rb, Sr, Pb, Zn, V, Zr, Cr, Co, Ni, Ga and Y.

RESULTS AND DISCUSSIONS

Radiometric Analysis:

Since the time of nucleosynthesis, radioisotopes with long half-lives have survived in detectable amounts till today. These primeval or primordial isotopes have been the subject of intense study in geochemistry because of their importance to heat flow studies. Uranium and thorium in nature give rise to radioactive decay chains consisting of several isotopes. Together with the isotope potassium-40, the naturally occurring radioactive materials (NORM) are of interest for many other reasons including for the experiments in particle physics.

Data of the radiometric analysis in table (1) indicated that these level of radioactive elements in the studied clay sediments is in the permissible limits in accordance with the Egyptian laws of the radioactive levels of the elements. So, the studied sediments considered safe and free from any radioactive elements.

Table 1: Radiometric analysis of the studied clay sediments

Clay sediment	Equivalent Uranium(eU)(ppm)
Kalabsha - kaolinite	7
Abu-Tartur-bentonite	3
El Hafafit - vermiculite	1

Table 2: Physical and chemical characteristics of the studied clay sediments

				AEC ***	Mechanical An				
Sample	pH *	EC *	CEC **				Textural Classes		
					Coarse Sand	Fine Sand	Silt	Clay	
Kaolinite	7.20	0.43	12.8	9.58	3.35	11.44	23.67	61.54	Clay
Bentonite	6.44	2.83	71.0	11.66	17.51	15.49	13.28	53.72	Clay
Vermiculite	7.00	1.40	90.0	4.96	13.38	11.49	22.49	52.64	Clay

^{*} Soil water (1:5)

^{**} CEC for kaolinite ,montmorillonite and vermiculite = 3-15 , 60-150 and 100-150 Meq/100g respectively, Wilson (1994).

^{***} AEC for kaolinite ,montmorillonite and vermiculite = 7-20 , 20-30 and 4 Meq/100g respectively, Wilson (1994).

Physical and Chemical Characteristics:

Some general characteristics of the performed clay sediments listed in Table (2). From this Table it is clear that:

- · The textural classes was clayey ,this attributed to the geological nature of the parent sediments.
- Chemical analyses of the saturation extract indicated that the sediments were neutral reaction, non-saline and values of C.E.C and A.E.C. in the same range of published data, Wilson (1994).

Mineralogical Characteristics:

XRD Analysis:

The XRD patterns of the studied clay samples (Fig.3) as well as the modal mineralogical composition calculated according to Griffin (1967) for semiquentitative interpretation of mineral abundance from XRD results (Table 3) represented.

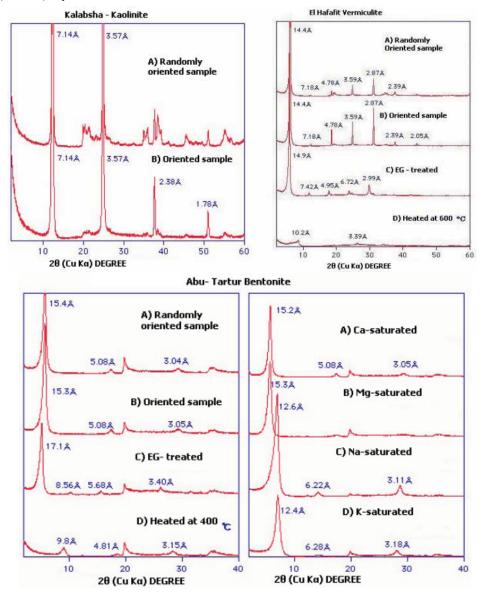


Fig. 3: X - ray diffraction patterns of the studied clay sediments

Table 3: Semi quantitative analysis of mineralogical composition of the studied clay fraction.

Sediment	Kaolinite	Montorlinite	Illite	Verniculite	Gypsum	K_2CO_3	Feldspar	Quartz	Others
	(%)		(%)		(%)	(%)	(%)	(%)	(%)
Kaolinite	80							5	15
Bentonite	5	56	9		5			11	14
Vermiculite				57		7	6	13	17

Table 4: I.R spectra interpretation for the studied clay sediments compared with the published data

Kaol.	Kaol.well	Mont.camp.	Ill.Musco.	III.	Vermiculite	H2O and OH	Kalabsha	Abu-	El
Disord.	Cryst.	Bert.	like	Phengite-like				Tartur	Hafafi
3697	3697				3694		3696		
3653	3652						3655		
		3627	3627	3640			3622	3626	
3621	3620			3622					
					3571				
								3420*	3424
						2930(H2O stretch)	2926		2924
						2380(O-H)	2371	2370	2370
						2350(O-H)	2341		
						1638(H2O-bend)	1633	1638	1640
1108	1108						1115		
1035	1036	1038					1035		
			1026	1024				1027	
	1014						1008		1008
	936								
915	916	918	915	916			914		
793	795	788	803				793	797	
754	758		754	754			754		
699			694				694		
					675				677
541	540		536				539		
		522		527				522	
478	474	467		475			470	468	
					458				459
				421			429	422*	

^{*} Vibrational frequencies at 3420 cm⁻¹ and 422 cm⁻¹ are related to the non-crystalline hydrated Al- silicates of variable composition, farmer(1974)

The XRD patterns of the studied clay samples revealed that kaolinite are the sole clay mineral in Kalabsha. Its percentage reached 80% while the rest of the sample is quartz 5 % and others (15 % iron oxides and accessory minerals). This result is in a good agreement with that of Akarish (2000) and Afifi (2003).

On the other hand, the XRD pattern revealed that the bentonite sample is composed of clay minerals mixture including kaolinite (5%), montmorillonite (56%) and illite (9%) in addition to quartz (11%) and others (14%). The bentonite sample proved to contain a small percentage of gypsum (5%). Moreover, it contains higher percentage of montmorillonite relative to the kaolinite percentage, almost the same mineralogical composition is shown by kadry and ashraf (2001) during their study in the same region.

However, the XRD data of El Hafafit vermiculite showed that the vermiculite clay mineral is the sole clay mineral (57%) plus carbonates (7%), feldspars (6%), quartz (13%) and others (17%).

Infrared Analysis (IR):

The infrared spectra of the studied clayey samples represented in Fig. (4) and the analytical infrared data are tabulated in Table (4). The infrared spectrum of kaolinite sample compared to those of the well-crystallized and disordered kaolinites. While the bentonite sample infrared spectra compared to infrared spectra of montmorillonite (Otay) and illite. The infrared spectra of El Hafafit vermiculite sample compared to that presented in the literature (Wilson, 1994). From these spectra, one can conclude that:

- There is a good matching between the infrared spectra of Kalabsha kaolinites with the infrared spectra of the disordered kaolinite. This is due to the presence of vibrational frequencies at 694 cm⁻¹ and 470 cm⁻¹, which characterize the disordered kaolinite, and the absence of the vibractronal frequency at 936 cm⁻¹, which characterizes the well crystalline kaolinite.
- The benotnite and vermiculite samples characterized by the vibrational frequency at 3420 cm⁻¹ and 422 cm⁻¹ that are related to the non-crystalline hydrated Al silicates of vibrational composition (imogolite).
- The Egyptian clay samples are characterized by the presence of vibrational frequencies at 2930 cm⁻¹ and 2350 cm⁻¹ (O-H) and 1638 cm⁻¹ (H₂O-bend).
- All the infrared spectra of the Egyptian clay samples namely kaolinite, bentonite and vermiculite are
 matching well with the infrared spectra of the analogous clay international standards.

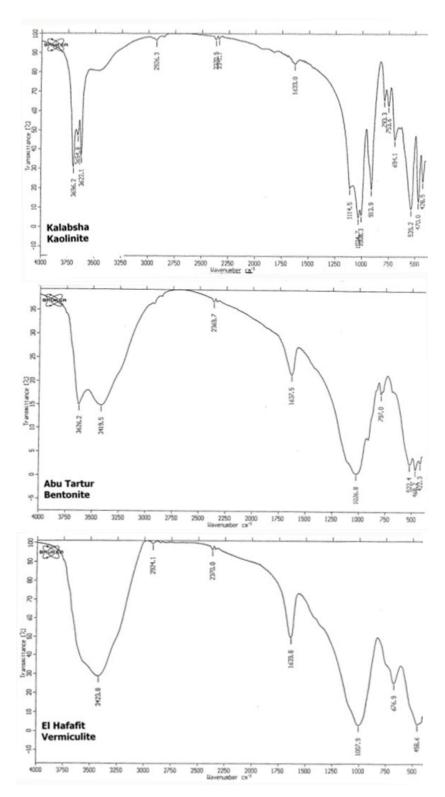


Fig. 4: I.R spectra patterns of the studied clay sediments

Differential Thermal Analysis (DTA):

The DTA curves of the Egyptian kaolinites with the DTA curve of the international kaolinite are well matching (Fig. 5) in the range from 0-800 °C. However, the Egyptian bentonitic sample shows fairly matching with the montomorillonite of Missisipi, Wyoning-1 and Wyoming-2, U.S.A. and with the International kaolinite. They seem closer to the montmorillonite of Wyoming-2. Besides, Hafafit vermiculite shows close similarities with West Chester of Pennsylvania rather than with the vermiculite of Kenya. In addition, Table (5) represents the DTA phase characteristics of the studied Egyptian clays according to Mackenzie (1970).

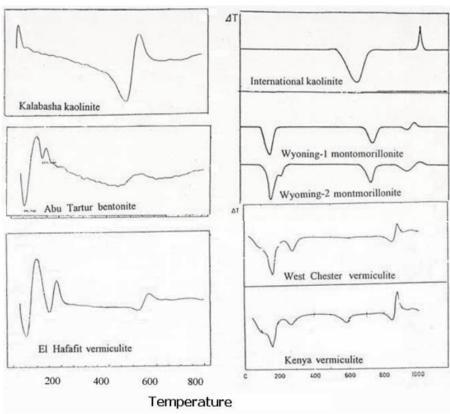


Fig. 5: DTA curves of different Egyptian sediments compared with Mackenzie (1970)

Table 5: DTA phase characteristics of the studied Egyptian clays.

DTA Data Peaks (,	Phase Characteristics
Endo Minerals	Exo thermic	Phase Characteristics
40-66		Dehydration (loss of adsorbed water).
	96-109	Oxidation of organic matter.
118-152		Dehydration of gypsum.
	192	Dehydration of vermiculite.
237		Dehydration of goethite.
	257	Exothermic. peak of cristoballite silica mineral.
406-490		Dehydroxylation and decomposition of halloysite (sub-group of kaolinite).
	511	Separation of A 1,0,
522		Quartz conversion.
	527	Exothermic peak of montmorillonite.
-	569	Exothermic peak of vermiculite.
630-673		Dehydroxylation & decomposition of kaolinite structure.
	632	Dehydroxylation of montmorillonite
714-722		Dehydroxylation of structure OH groups.
757		Decomposition of carbonate.
	774	Decomposition of Mg -carbonate.
787		Beginning of crystallization of the amorphous dehydroxylation products.

Table 6: Chemical composition of kaolinite, bentonite and vermiculite clay samples

Sample	SiO ₂	Al_2O_5	TiO ₂	P_2O_5	FeO	Fe_2O_3	Na_2O	K ₂ O	CaO	MgO	L.O.I.	Total
Kaolinite	46.90	32.30	1.29	0.03	*	0.79	0.48	0.16	1.40	1.20	14.69	99.24
Bentonite	58.00	14.50	0.62	0.05	0.20	3.95	0.43	2.68	1.72	0.30	14.06	96.51
Vermiculite	39.51	15.30	0.08	0.06	0.32	3.16	1.68	3.26	4.50	12.30	17.10	97.27

L.O.I. =Loss on ignition at 1000°C for 24 hours. * = Under limit of detection.** = Include 4.00 % SO₄. *** = Include 3.00 % CO₃.

This table confirms the presence of iron oxides (geothite), organic matter gypsum and carbonates in the studied clay minerals. This result also confirms the previously calculated modal mineralogical composition.

Chemical Analysis:

Results of Major Oxides Analysis:

The results of major oxides analyses of the studied clayey samples tabulated in Table (6). From this table it is clear that:

- The kaolinite is characterized by higher percentages of alumina (32.3%) and silica (46.9 %) if compared with bentonite (14.5%) and (58.0%) respectively. On the contrary, the vermiculite is characterized by lower percentage of both alumina (15.3%) and silica (39.51%).
- The bentonite sample is characterized by high concentration of Fe₂O₃ (3.95 %) relative to kaolinite (0.79 %). However, the Fe₂O₃ concentration in the vermiculite sample is fairy high (3.16 %).
- The bentonite sample has higher distribution of alkali oxides namely Na_2O (0.43 %), K_2O (2.68 %) and CaO (1.72 %) relative to (0.48 %), (0.16 %) and (1.4 %) in kaolinites respectively.
- The vermiculite sample is characterized by its higher content of Na₂O (1.68%) K₂O (3.26%) (CaO (4.5%) and specially MgO (12.3%)
- All the analyzed clay samples are characterized by the presence of high loss on ignition percentages.

On the other hand, the major oxides analysis was used in the calculation of mineralogical composition (Salem, 1990) and Afifi (1991) from the chemical analysis (Table7). From this table and table(3) one can notice that there are general agreement between the modal mineralogical compositions of the Egyptian Kaolinite, bentonite and vermiculite samples with the calculated ones.

Table 7: Calculated mineralogical composition from chemical analysis.

Sample	Ka	Mont	Illite	Verm	Gyp	Carb	Feld	Qz	Othes
Kaolinite	78							9	18
Bentonite	5	48	13		5			15	14
Vermiculite				70		6	7	10	17

Ka = Kaolinite. Mont = Montomrilonite. Verm = Vermiculite. Gyp = Gypsum. Carb = Carbonates. Feld = Feldspars.Qz = Quartz

Trace Elements Analysis:

The data of the trace elements analysis for the studied clay samples represented in Table (8). From these data, it is clear that: There are sharp differences between the distribution of some trace elements in kaolinite and bentonite from one side and vermiculite from the other side. For example, the distribution of V, Y, Zr and Ba is very low in vermiculite relative to the kaolinite and bentonite samples. On the other hand, the distribution of Cr, Ni in vermiculite is very high relative to those in the kaolinite and bentonite.

The presence of trace elements in the studied clays attributed to substitution, replacement or adsorption of these trace elements on the surface or in the lattices of the studied clay samples.

It is worthy to mention that the high content of V and Ga in the studied clay samples may render them to be natural resources for these two elements.

The high abundance of Ba and Zr may be due to the presence of barite and zircon minerals respectively as accessory minerals in the studied clay samples.

 By comparing the results of trace elements analysis (Table 9) for the studied clay samples with those of El Tih Kaolinite (Akarish, 2000), Kalabsha kailinite (Afifi, 20003) and international shale (Mason, 1966), it is clear that:

The obtained trace elements analysis of the Kalabsha kaolinite samples is in a good harmony with the data published by Akarish (2000). Hower, there exist considerable differences with the analysis of trace elements offered by Afifi (2003) specially in the higher contents of V (557 ppm), Ga (121 ppm) and Ba (11101 ppm) and lower contents of Zn (11 ppm) and Sr (21 ppm). This may be due to sampling.

Table 8: Trace elements analysis of the studied clay samples in (ppm)

Element	Kaolinite	Bentonite	Vermiculite
V	142	110	49
Cr	147	106	702
Со	30	25	26
Ni	34	43	406
Cu	82	41	28
Zn	90	56	55
Ga	7	8	7
Sr	215	202	160
Y	104	65	14
Zr	258	172	33
Nb	5	8	22
Ва	5127	3311	953
Pb	17	20	18
Rb	11	14	8

Table 9: Published trace elements analysis for some clays:

Locality	V	Cr	Co	Ni	Cu	Zn	Ga	Sr	Y	Zr	Nb	Ba	Rb
El Tih Kaolinite (Akarish, 200)	144	164	4	26	-	-	38	-	-	679	-	-	4
KalabshaKaolinite Afifi, 2003)	557	286	7	36	-	11	121	21	21	701	26	11101	2
International Shale (Mason, 1966)	130	90	19	68	45	95	19	300	26	160	11	580	140

The trace element data obtained for the Abu Tartur bentonite samples are in agreement with the trace elements analysis of the international shale (Mason, 1966) for Cu, N,V, Cr Cu, Zn, Ga, Sr, and Nb. However, they show disagreement in the analysis of Y, Zr and Ba (higher in the studied samples) and Rb (higher in the international shale).

Conclusions:

This study recommends and confirms that utilization of the studied clay sediments are safe for different environmental applications such as disposal of waste radioactive materials, removal of toxic and heavy elements from low quality water and soils, loaded with different nutrients to add to the soil to supply the plant with different nutrients.

Because the studied clay sediments have high content of V and Ga they qualify to render them to be natural resources for these two important elements.

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