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STUDY OF CHEMICAL ELEMENTS IN BLACK SAND AND THEIR RELATIONSHIP WITH SOIL VARIABLES ON EL-BROLIS –LAKE COAST –EGYPT.

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Key Wards ; Black sand . El –Brolis , Rashid , Trace element.

ABSTRACT.

Three profiles were selected number 1,2 from EL-Brolis –Lake coast and profile number 3 from Rashid where the samples are black sand and every profile contain tow layer of surface and subsurface Physical and chemical properties of the black sand are determined where the texture is sand Soil reaction (pH) is alkaline, $CaCO_3$% ranges from 0.55 to 1.10 % , organic matter varied from 1.74% to 4.04%, salinity of black sand is high varied from 2.27 to 22.29 dSm^{-1}. The cation and anion(mmolc/l) followed this order $Cl^{-} > Na^{+} > K^{+} > SO_4^{--} > Ca^{++} > Mg^{++} > HCO_3^{-} > CO_3^{--}$. Total and extractable of trace elements in international limits values and NPK in the studied area varied form deficient to sufficient.

This study determine the concentration of trace elements (Total & extractable) and find a relation between soil variables and the content of trace elements.

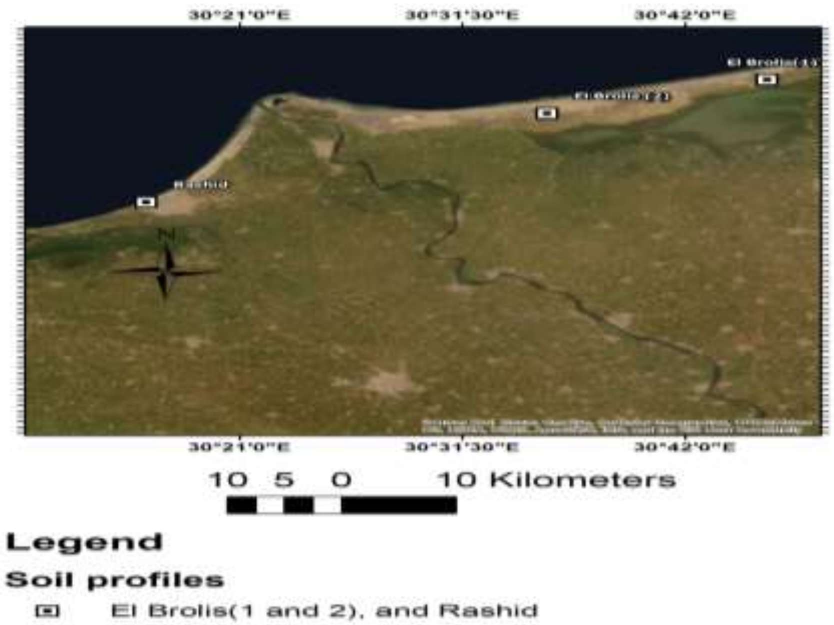

Fig.(1)Location of the studied area

INTRODUCTION

The Egyptian black sands placer deposits on the Mediterranean Coastal Plain contain many mineral species as they have been derived from igneous and metamorphic rocks **(Higazy and Naguib (1950).**

Many studies were carried out dealing with the mineralogical composition, grain size distribution, origin of the sediments as well as their economic considerations. Black sand constituents include six heavy economic minerals; namely magnetite, ilmenite, monazite, zircon, rutile and garnet. Monazite, zircon and rutile minerals contain number of elements necessary for the nuclear industry e.g. uranium, thorium, zirconium, hafnium, titanium and rare earths elements. Thus, the evaluation of these raw materials in the Egyptian black sands placer deposits would be calculated on the basis of the reserves of monazite, zircon and rutile mineral content in localities along the Mediterranean Coastal Plain; namely Rosetta, Baltim, Damietta and north Sinai. **(Dabbour et al., (1990)**

Late Miocene and before the completion of the High Dam in May 1964, the River Nile was discharging huge quantities of sediments during the annual flood seasons in the Mediterranean Sea. These sediments were the final products of the disintegrated materials from the two main drainage areas of the Nile Basin which cover an area of about 3,000,000 km^2 i.e. The Equatorial Plateau (igneous rocks) and the Ethiopian Plateau **(Said,(1981).**

Missak, and Attia, (1981). Chosen four localities for geological reserve evaluation for monazite, zircon and rutile are considered to be the principal black sands deposits. The first locality is on both sides of Rosetta promontory. It extends from Idku Lake outlet to El Burrullus Lake openning. This stretch is about 70 km long and its width varies from about 200 m to about 5000 m with an average width of about 800 m. The area is characterized mainly by beach deposits except west Rosetta outpouring sector which has coastal plain sand dunes. The depth of the black sands in this area reaches about 9 m. Beyond this depth, the sand fraction decreases to be less than 40% while the clay fraction constitutes the 193 major percentage. Above the mentioned depth, the sand fraction generally exceeds 60% of the sediments.

The second locality is the coastal plain sand dune belt in which the heavy minerals content reaches up to about 35% and covers the area from Burg El Burrullus village eastward to El Gharbia Main Drainage, a stretch of about 15 km long and average width of about 800m. The height of the sand dunes in this area reaches up to 15m, however, an average height of 5 m will be considered. Assuming that the beach sediments under the sand dunes reach about 10m depth, the thickness of the deposit in this area will be considered as 1 5 m.

The third locality is the north western part of El Manzalla Lake and the beach area just east of Damietta outpouring. The depth of this deposit will be 10 m and the area is about 30 km^2. This area is characterized by a series of parallel sand bars called "Barr" trending generally northwest and are separated by longitudinal lagoons called "Tawal". The mechanism of formation of these parallel sand bars was attributed to the result of the accretion of the bottom sediments of the continental shelf by the wave action and the continuous accumulation of these sands till the sand bar became exposed on the surface of the sea water leaving a longitudinal lagoon behind it.

The last locality is the north Sinai coastal plain sector which extends between the eastern openning of El Bardawiel Lake at El Zaraniq in the west and El Arish town in the east. This stretch is about 20 km in length and about 500 m width It is characterized by beach deposits lined from the south by north Sinai sand dune belt .. The depth of the deposit in this area is about 10 m. **(Missak, and Attia,(1981).**

Monazite Mineral:

The mineral monazite is the world supply source for both rare earth elements and thorium. Chemically the mineral is an orthophosphate of rare earth elements and thorium; (REE, Th)PO_4. The rare earth oxides represent 60% of the mineral and consists mainly from the elements which have low atomic numbers (e.g Lanthanum ”La”, Cerium ”Ce”, Praseodymium ”Pr”, Neodymium ”Nd”) and known as light rare earths group. The predominant component of the rare earths in monazite is cerium, which often constitutes up to 45% of the total rare earths content, so the rare earths known as “cerium group” **(Ellis 1994)**. The rare earth distribution in monazite was variable depending upon their location, i.e. the rare earth elements from different locations had not exactly the same distribution (Table 1).

Table (1): Rare Earth Distribution in Monazite from Different Locations (Gupta and Krishnamurthy 2005)

Rare earth oxide	U.S.A		India	China	Brazil	Australia			Egypt (Mostafa 2009)
	Idaho	Florida				Mount Weld	Capel	Queensland	
La	26.23	17.50	23.00	23.35	24.00	26.00	23.9	21.50	23.2
Ce	46.14	43.70	46.00	42.70	47.00	51.00	46.0	45.8	44.7
Pr	6.02	5.00	5.50	4.10	4.50	4.00	5.0	5.3	4.7
Nd	16.98	17.50	20.00	17.00	18.50	15.00	17.4	18.6	17.6

Thorium "Th" together with the heavy rare earth element "yttrium Y" are usually present substituting for cerium, etc, so, thorium amount ranges from 4% up to 12% ThO_2 are usually reported. Monazites are also reported to be contain uranium which ranges from trace amounts up to values as high as 1.0% U_3O_8 **(Gupta and Krishnamurthy 2005)**.

Monazite Occurrence and Distribution:

Egyptian monazite was found in beach sands and sand dunes along the Nile Delta recent shore line in a zone extending from Rafah to Abo Qir, East of Alexandria. It was found also in sand bars isolating the lagoon lakes of El-Bardawil, El-Manzalah, El-Burullus and Edku from the Mediterranean Sea **(Mostafa 2009)**. However, these black sand deposits have actually been carried by the River Nile and laid down in the Mediterranean Sea and later transported to its shores by water currents, winds, waves or others. The chemical composition of the Egyptian and the different monazite sands was shown in table (2).

Table (2): The Egyptian and Different Monazite Sands Composition

Constituent, wt%	Egyptian (Mostafa 1995)	Australian (Gupta 2005)	Indian (Gupta 2005)
RE_2O_3	61.17	58.5	58.60
ThO_2	5.75	6.4	8.8
P_2O_5	27.8	27.5	30.1
SiO_2	0.7	2.83	1.7
Others	4.58	4.77	0.8

PHYSICAL PROCESSING OF BLACK SANDS:

Monazite sand concentrate was obtained as a by product during the successive separation and concentration of the different economic minerals through physical processing techniques for black sands. These separation procedures utilize a combination of the following well established industrial techniques **(Gupta and Krishnamurthy 1992)**:

1- Gravity separation using shaking tables (utilizing differences in specific gravity , shapes and grain size in fig.2.

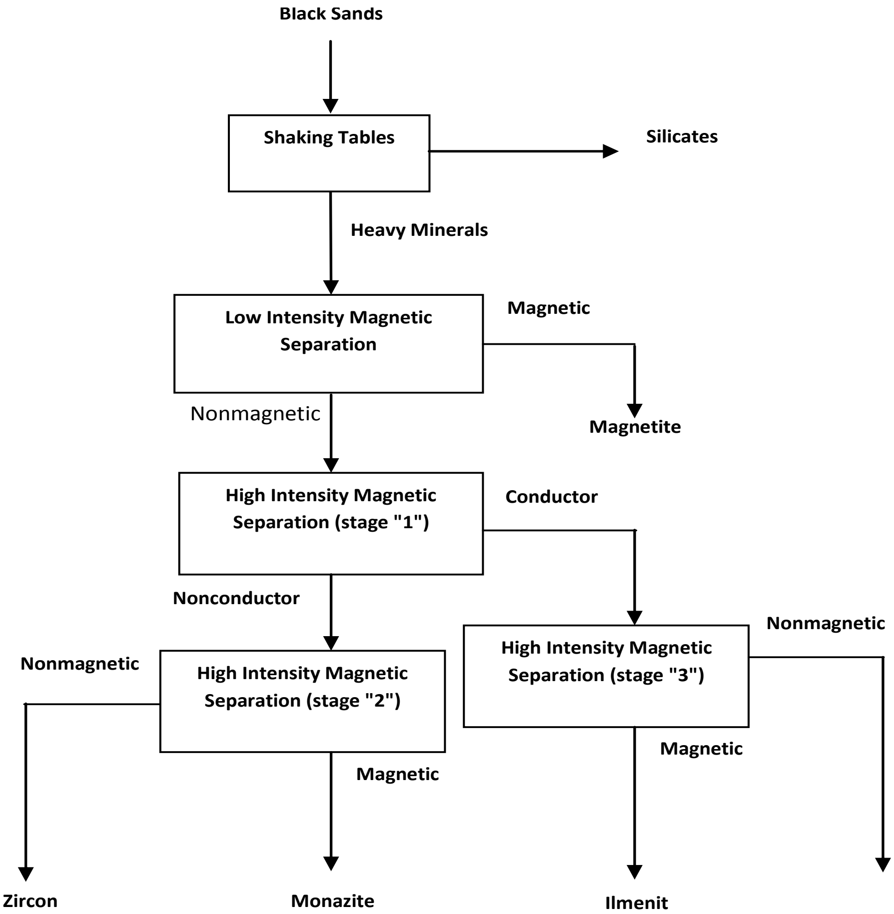

Fig. (2): Separation of Valuable Minerals and Monazite from Black Sands by Physical Methods

MATERIALS AND METHODS

Soil samples analyses.

Textured of the soil samples was determined with the dry sieving method **(Piper 1950) .**

- $CaCO_3$ content was determined volumetrically using Collin's calcimeter according to **Jackson (1973).**
- Organic matter content was determined by the method outlined by **Jackson (1973).**
- Determination of pH in the soil extract was carried out by Beckman glass electrode pH – meter, **Black (1983).**
- Electrical conductivity (EC) of the soil saturation extract as well as soluble anions and cations were determined following the methods described by **Jackson (1973).** For convenience, CO_3^{--},Cl^-, HCO_3^-,

were determined titrimetrically while SO_4^{--} was determined gravimetrically by precipitation as barium sulfate.Soluble Ca^{++} and Mg^{+} were determined titrimetrically using the versenate solution while Na^{+} and K^{+} were determined by flame Photometry, as described by **Black (1983).**

- Cation exchange capacity (CEC) and exchangeable cations were determined following the methods described by **Jackson (1973).**
- Total trace metals contents in the soil samples (Zn, Cu, Ni, Co, Cr and Cd) were determined by the Ionic Coupled Plasma (ICP), after digestion of the samples with a ternary acids mixture of HNO_3, H_2SO_4 and $HClO_4$, as recommended by **Hesse (1971).**
- Chemically – extractable amounts of the same elements were extracted from soils by Diethelene triamine pentaacetic acid (DTPA) and determined by Inductively Coupled Plasma, (ICP). **Lindsay and Norvell (1978).**

RESULTS AND DISCUSSION

1- Characterization of the studied soils;

Studied of the soil texture were indicated from Tables (3 and 4) which the result reveal that the soil samples is sand varied form very coarse sand to fine sand (VCS to FS) .Soil reaction in this studied soil is alkaline as indicated by pH values which ranged from 8.09 to 8.74 .Calcium carbonate content ranes from 0.33 to 1.10 % .The organic matter ranged form 3.01 to 4.04 % .CEC for the studied soils ranges from 1.18 to 2.74 mmol /100 g. Soil salinity is very high varied from 2.27 to 22.29 dS/m this due to the proximity of the profiler to the seashore. The cations and inions of the studied soil are generally take this order $Cl^{-} > Na^{+} > K^{+} > SO_4^{--}$.$Ca^{++} > Mg^{++}$.$HCO_3^{-} > CO_3^{-}$

Thus to use this regions of black sands in agriculture, it must be treated to eliminate this salinity.

Table (3)Dry sieving of the studied soil on EL-Brolis Lake coast-Egypt.

Location	Profile .No.	Sample No.	Depth (Cm)	VCS %	CS %	MS %	FS %	VFS %	SI+CL %
1 - El-Brolis									
31° 30′ 20.2″ N	**1**	**1**	**0 – 30**	**1.33**	**7.59**	**21.49**	**62.26**	**6.43**	**0.90**
30° 45.″ 54.2″ E		**2**	**30 – 60**	**2.93**	**7.73**	**59.92**	**28.38**	**0.42**	**0.62**
2-El- Brolis									
31° 27′ 13.3″ N	**2**	**3**	**0 – 30**	**3.66**	**9.89**	**14.61**	**54.60**	**13.83**	**3.41**
30° 35.″ 31.6″ E		**4**	**30 – 60**	**4.27**	**6.78**	**60.41**	**27.89**	**0.33**	**0.14**
3- Rashid									
31° 18′ 59″ N	**3**	**5**	**0 – 30**	**0.52**	**0.20**	**3.55**	**87.60.**	**5.80**	**2.37**
30° 16.″ 38.1″ E		**6**	**30 -60**	**0.20**	**0.15**	**17.56**	**76.76**	**4.31**	**1.02**

.(VCS)Very coarse sand. (CS) Coarse sand , (MS 0 Medium sand, (FS) fine sand (SL) Silt , (CL) clay .

Table (4) Chemical properties of the studied soils

Prof.	Samp.	Depth	pH	EC	$CaCO_3$	O.M	Cations (Me/l)				Anions (me/L)				CEC
NO.	NO.	(cm)		ds/m	%	%	Na^+	K^+	Ca^{++}	Mg++	CO_3^{--}	HCO_3^-	Cl^-	SO_4^{--}	Me/100g
1- El- Brolis	1	0 – 30	8.15	11.97	0.55	3.47	88.48	17.09	10.08	5.15	0.00	0.36	112.50	6.88	1.5
	2	30 – 60	8.09	22.29	0.76	4.04	171.98	23.98	19.90	9.85	0.00	2.79	199.00	21.13	1.5
2- El- Brolis	3	0 – 30	8.34	13.66	0.65	3.41	96.47	25.28	11.53	5.06	0.00	1.55	110.60	24.42	2.74
	4	30 – 60	8.35	15.59	0.33	3.99	110.87	25.28	13.08	5.97	0.00	1.52	139.99	14.39	1.18
3- Rashid	5	0 – 30	8.73	2.27	1.10	1.74	20.02	1.21	2.50	0.50	0.00	0.60	12.00	10.13	2.54
	6	30 – 60	8.18	3.02	1.10	3.01	22.27	1.38	3.10	2.30	0.00	1.20	15.90	13.07	2.54

2- Total trace elements in the studied Black sands.

Data in table (5) listed some trace metals contents of Cd, Co, Cr , cu ,Fe , Ni , pb and Zn. The vertical distribution of these elements in all profiles as Cd, Co and Cr metals content decrease from top to bottom and the highest values in the surface layer while the lowest values were in the second layer but as for Cu metal in profile 1. the lowest value in the surface layer 3.16 mg/kg but the highest value in the second layer was 3.38 mg/kg .Cu in the profile 2 the vertical distribution the highest value 7.58 mg/kg in the surface later and the lower value in the subsurface layer 0.76 mg/kg .Also in profile 3. the lower value in the surface layer and the higher value in the subsurface layer. Fe metal content decrease by increasing the depth of the profiles 1,2 but in profile 3, Fe content decrease by increasing the depth of the profile.Ni content increasing by increasing the depth of profile 2,3 but in profile 1 the concentration of Ni metal increasing by increasing the depth of the profile. Pb metal content increasing by the depth in all profiles . the highest value in sub surface layer of profile 2 . 46.47 mg/ kg but the lowest value in the surface layer in the profile 10.81mg/kg. in the end Zn metal content in profile 1,3 the content increase by the depth of the profiles. But in profile 2 the content of Zn metal decrease by increasing the depth of profile. the Maximum permissible concentrations of trace elements reported by (Kabata-Pendias and Pendias 2001) are : Cd (cadmium) 5 mg/kg, Co (cobalt) 50 mg/kg, Cr (chromium) 100 mg/kg, Cu (copper) 100 mg/kg, Ni (nickel) 100 mg/kg, Pb (lead) 100 mg/kg, and Zn (zinc) 300 mg/kg.

Table (5)Total trace elements content of black sand in the studied area of El-Brolis Lake coast –Egypt.

Prof.	Samp.	Depth	Cd	Co	Cr	Cu	Fe	Ni	pb	Zn
NO.	NO.	(cm)	mg/kg							
1-El-Brolis	1	0 – 30	2.77	20.9	108	3.16	14680	11.68	14.76	31.65
	2	30 – 60	2.42	20.5	45.6	3.38	11720	16.21	22.66	76.35
2-El-Brolis	3	0 – 30	0.98	30.7	198	7.58	25.860	30.44	5.91	59.87
	4	30 – 60	0.50	7.34	53.3	0.76	7133	8.68	46.47	17.29
3- Rashid	5	0 – 30	0.88	10.7	52.5	1.09	10520	20.26	0.81	22.17
	6	30 – 60	0.75	4.83	37.8	2.70	10820	7.35	12.11	38.43

3- Chemically extractable of trace elements in black sand in the studied area of EL-Brolis Lake coast –Egypt.

Data in table (6) listed concentration of available trace elements in the studied area black sands Cd, Co, Cr , cu ,Fe , Ni , Si and Zn the vertical distribution of the metals show Cd metal in profile 1, decrease by increasing the depth of profile. But in profiles 2,3 Cd metal concentration increase by increasing the depth of profiles. In Co metals the distribution increasing by increasing the depth of all profiles ,in Cr , Fe , Ni , Zn and Cu metals the concentration decreasing by increasing the depth of all profiles except Cu and Si metals in profile3. the surface layer of Cu and Si content lower thane the subsurface layer . The maximum permissible concentrations of extractable of trace metals in soil are the following,: Pb – 6,0 mg/kg and Cr - 6,0 mg/kg Ni – 4,0 mg/kg Co – 5.0 mg/kg Zn – 23,0 mg/kg Cu – 3,0 mg/k**g** Kabata-Pendias and Pendias 2001.

Table (6) Chemically extractable of trace elements in black sand in the studied area of EL-Brolis Lake coast –Egypt.

Prof.	Samp.	Depth	Cd	Co	Cr	Cu	Fe	Ni	Si	Zn
NO.	NO.	(cm)	mg/kg							
1-El-Brolis	1	0 – 30	0.063	0.090	0.032	0.493	26.98	0.170	23.84	2.63
	2	30 – 60	0.024	0.150	0.004	0.397	11.51	0.154	29.28	1.42
2-El- Brolis	3	0 – 30	0.028	0.140	0.037	0.535	36.84	0.172	15.03	1.26
	4	30 – 60	0.036	0.145	0.036	0.347	12.87	0.169	23.90	1.43
3- Rashid	5	0 – 30	0.091	0.074	0.032	0.369	47.36	0.190	15.80	1.32
	6	30– 60	0.095	0.111	0.009	0.419	45.94	0.006	5.01	1.70

4 - Correlation between trace element and soil variables :

Significant correlations were calculated between trace element and some physical and chemical properties.

The correlated highly significantly positively between EC / Na^+ was (r =0.997), EC/ Ca^{++} (r =o.997), EC/ Mg^{++} (r =0.978),EC/K^+ (r= 0.912),EC/Cl^{-1} (r =0.997), EC/ OM % (r=0. 861),EC/HCO_3^{-2} (r=0.737),EC/SO_4^{-2} (r=0.553) ,EC/ total Cr (r =o.749), EC/ total Al (r =0.588), and EC/ total Ca (r =o.950). EC / total. Co (r =0.809), $CaCO_3$/ K^+ (r =0.859), OM%/ Na^+ (r =0.837), OM%/K (r =0.833), OM%/Ca^{++} (r =0.844), OM%/ Mg^{++-} (r =0.886), OM%/ Cl^{-1} (r =0.863) ,Na^+ / Ca^{++} (r =o.999), Na^+/ Mg^{++} (r =0.983), Mg^{++}/Cl^{-1} (r =0.994), Na^+/ K^+ (r =0.879), K^+/ Ca^{++} (r =0.883), K^+/Mg^{++}/ (r =0.828), K^+/Cl^- (r =0.903), Ca^{++}/Mg^{++} (r =0.984), Ca^{++} / Cl^- (r =0.993), Mg^{++}/ Cl^- (r =0.976), pH / total Li (r =0.684), pH/ total. Co (r =0.684), pH^- /total Ca (r =0.652), pH/SO_4^{2-} (r =0.696). The statistical analysis revealed that correlated significantly positively between pH/total Cd (r =0.563).

Data presented in Table (7), indicated that soil Nitrate-N values were ranged from 17.5 to 66.5, according to Soil **Mukashema (2007)**, soil Nitrate-N values in the area Fall in the ranges in sufficient level, expect profile No.1 fall in low level.($N\text{-}NO_3$ < 19 mg/kg) very low , (19 -37) low, (38 – 51) moderate, (52- 70) high , > 70 mg/kg) very high. (Extraction method)

Table (7) NPK(mg/kg) in the studied area

Profile No.	Sample No.	P	K	N- No_3
1	1	4.96	106.7	17.5
	2	4.76	110.6	21
2	3	4.53	101.3	63
	4	5.21	101.9	66.5
3	5	5.93	43.7	64.4
	6	6.43	46.6	66.5

While Olsen-P Soil were ranged from 4.76 to 6.43 mg/kg refer that all profiles are exit in deficient level. K availability (mg/kg) were ranged from 43.7 to 110.6 refer that profiles are exit in sufficient level expect profial No.3 fall in deficient level. Where,the critical level of them N as nitrate in soil solution =50 mg/kg , P = 5 mg/kg and K =80 mg/kg but they are differing among soils.

Based on the soil analysis, fertility stauts, it is preferable to use the area for agricultural use. It is preferable to applying different fertilizers with irrigation water in order to obtain the highest crop productivity

CONCLUSION:

1-The soil texture of the studied soil samples is sand. soil reaction is alkaline calcium carbonate ,organic matter percent and CEC is very low. The cationic and anionic ions take this order. Cl^- > Na^+ > K^+ >SO_4^{--} > Ca^{++}> Mg^{++} > HCO_3^- > CO_3^{--}

2- Total and extractable trace elements in international limits or lesser. NPK in the studied area varied from deficient to Sufficient . the Egyptian black sands need treatment to used in agriculture.

3- The Egyptian black sands contain monazite mineral which consider the source of rear earth elements and thorium. Monazites are also reported to be contain uranium which ranges from trace amounts up to values as high as 1.0%

4- Must be removal this radio active elements as uranium , thorium, zirconium, hafnium, titanium from black sands.

5- To eliminate this radio active elements its very expensive.

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دراسة بعض العناصر الكيميائية فى الرمال السوداء وعلاقتها بمتغيرات التربة على ساحل بحيرة البرلس – مصر

عبدالسلام محمد عبدالسلام علوة

قسم كيمياء وطبيعة الأراضى – شعبة مصادر المياه والأراضى الصحراوية–

مركز بحوث الصحراء – المطرية – القاهرة.

تم اختيار ثلاث قطاعات من الرمال السوداء قطاعين من ساحل بحيرة البرلس وقطاع من ساحل رشيد واظهرت نتائج التحاليل الأتى : –

1– قوام التربة رملى وان التربة قلوية التفاعل ونسبة كربونات الكالسيوم تتراوح مابين 0.55 – 1.10% ونسبة المادة العضوية تتراوح ما بين 1.74– 4.04% وملوحة التربة تتراوح مابين 2.27 – 22.29 dsm^{-1}.

2– وكان تركيز الكاتيونات والانيونات الذائبة كالاتى :

$Cl^{-} > Na^{+} > K^{+} > SO_4^{--} > Ca^{++} > Mg^{++} > HCO_3^{-} > CO_3^{--}$

3– وان التركيز الكلى والمستخلص للعناصر الصغرى للتربة فى مستوى الحدود المسموح بها او اقل .

4– واتضح أيضا أن الرمال السوداء تحتوى على معادن ذات اهمية اقتصادية كبيرة وتحتوى على عناصر مشعة مثل ا ليورانيوم وهذا يجعل من الصعب إستخدامها فى الزراعة الا بعد التخلص من العناصر المشعة وهذه عملية مكلفة تكلفة عالية اكثر مما سيعود منها عند زراعتها.

5 – لذا يقتصر التعامل مع الرمال السوداء على انها مصدر من مصادر الدخل القومى وذلك بفصل مافيها من معادن ثمينة وإستخدامها فى الأغراض الصناعية الهامة.