

Implication the Hydrchemical Features of Water Resulted from the Black Sand Processing and its Contamination by Radionuclides, Toxic and REEs

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Abstract: Mining of rare earth ores by water for physical upgrading resulted in hazard wastewater due to water-black sand interaction. The concentration of trace elements Mn, Zn, Cu, Cd, Zr, Fe and Pb illustrate that the studied washing water samples have permissible concentration suitable for drinking, laundry, irrigation, building, industrial, livestock and poultry except (Fe and Zr) elements. All water samples are unsuitable for drinking and irrigation and have iron and zirconium values higher than the recommended guideline values. Uranium, thorium and rare earths have values higher than the maximum permissible limits supported by organizations and recent studies indicating unsuitability for drinking water and other uses, in addition to their hazard on surficial, underground water and the surrounding plants. The most likely origin of water pollution is the lithological and mineralogical properties of rocks or minerals. Water quality and its suitability for irrigation and domestic purpose were examined by various hydrochemical parameters such as pH, total dissolved solids, total hardness, calcium, magnesium, sodium, potassium, bicarbonate, sulfate and chloride. These parameters were used to assess the suitability of water samples for domestic purpose by comparing with WHO. TDS, sodium adsorption ratio (SAR), percent sodium (Na%) and other parameters used for irrigation suitability assessment.

Keywords: Black sand, Wastewater, Trace and Rare earths elements.

1 Introduction

The Egyptian black sand deposits are discontinuously distributed along the northern Coastal Plain of the Nile Delta and Sinai Peninsula i.e. in the coastal stretch between Abu Qir to the west and Rafah to the east. These deposits contain strategic and economic minerals that include ilmenite, magnetite, garnet, zircon, rutile and monazite, leucosene, in addition to cassiterite. These minerals are useful for nuclear, metallurgical and engineering industries. Water is an essential resource for sustaining life and society. Freshwater is needed for the human diet, as well as for agricultural, industrial, and energy production activities. Freshwater constitutes only about 2.5 percent of all water on Earth [1]. By the year 2021, Egypt is projected to consume more than 20 percent than the currently available supply. Groundwater has been identified as the only promising freshwater resource to meet such growing demand. Groundwater currently provides only 7% of water demand in Egypt [2]. Recently, water authorities have given renewed attention to increasing the production of

groundwater in Egypt to improve the growing water consumption. However, the quality of available groundwater remains very important. Access to safe water resources is a crucial component of effective policy for health protection [3]. Water resource shortages have forced countries to use deferent water supply sources, such as groundwater, seawater, rainwater, riverwater, and wastewater [4,5]. Greywater includes water used by clothes and car washing machines and basins in kitchens and bathrooms in houses and mosques. Groundwater may be contaminated with heavy metals; for example, a risk of human exposure to heavy metals through groundwater used as a source of drinking water has been reported [6,7]. Several radionuclides in the radioactive decay chain starting from ^{238}U and ^{235}U are highly radiotoxic. On the other hand, these radionuclides may contribute appreciably to the dose received by humans through internal exposure due to their ingestion [8,9]. This work aims to evaluate the contamination of water used for physical upgrading of black sand by heavy metals, uranium and REEs and implicate its geochemical features.

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2 Experimental

2.1 Materials and Methods

Raw sands were subjected to different techniques separation of the economic minerals and monazite by physical methods (gravity, magnetic and electrical high tension traditionally used to determine some of the mineralogical characteristics and specification of the different mineral concentrates. One of the basic essentials for efficient table operation is a relatively uniform flow of pulp and wash water to the table. An increase in feed or grade cause broadening of the middling band towards the concentrate splitter position. Table capacity under steady pulp flow conditions is a function of the pulp density of the feed. Pulp must be maintained at a feed density to be sufficiently fluid to allow efficient stratification and to allow dilation between the riffles. Generally, treatment of granular sand requires a pulp containing less than 25% solids, whilst with slimes this could be as high as 30% solids.

In addition to the water in the feed pulp, water over the table for concentrate. This varies from a few liters to 100 liters per minute according to the nature of the feed material. Table uses 19 cubic meters of water in a period of four hours, an estimated 57 cubic meters of water is used per day on a 12-hour workday. It important to ensure that the water does not channel across the table and thereby hinder good stratification. It goes almost without saying that the wash water must be clean water. Whilst recycled water is often utilized, care must be taken to insure that no build up of deleterious slimes occurs as these rapidly destroy efficient tabling. Water is recycled which helps to concentrate and dissolve some beneficial and harmful elements. A sample of water was taken from water pool with dimensions (2*2.5*3) every four hour daily over the course of a week.

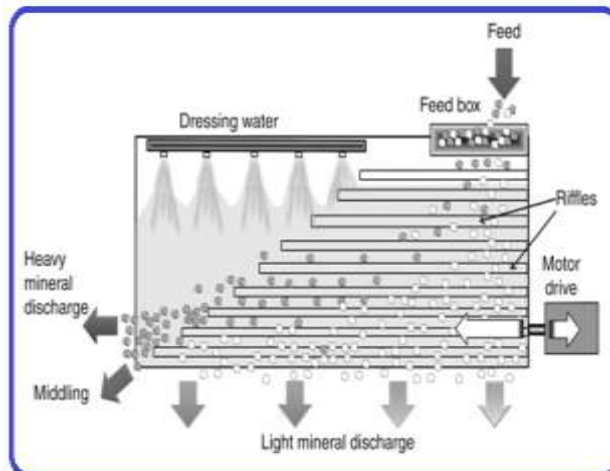
Although there are no hard and fast rules for table operation, the following points toward the correct setting for tables must be given:

*For a roughing operation: more water, more ore.

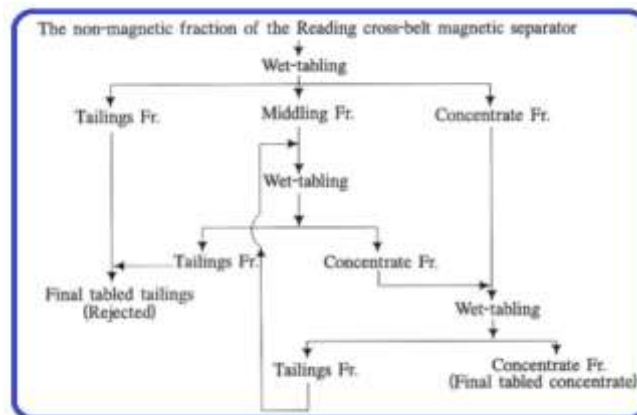
* For a cleaning operation: less water, less ore.

The full-size wilfley table No.20 were used. Taking into consideration all the studied parameters affecting the performance of shaking table, a circuit of three stages of wet-tabling were recommended to be carried out for the concentration off the required economic minerals from the non-magnetic fraction. In this circuit, the tabled middling of the first stage was reerated in a second wet- tabling stage.the product concentrates from the first and the second

stages were combind and retabled in a cleaning wet-tabling third stage.



Wet-gravity tabling circuit of the Reading cross-belt non-magnetic fraction.



Sketch of Wilfley shaking table structure.



Rough and cleaning operation for the wet tabling of the non- magnetic fraction Reagents and instruments.

2.2 Analytical Procedures

All the chemicals and reagents used in all different parts of this work are analytical grade. Double distilled water was used for preparing all standard solutions and reagents using Aquatron 4L/h (England). The hydrogen ion concentration for the solution was measured using Inolab digital pH-meter, level 1 (England), with an error of ± 0.01 at ambient laboratory temperature. The reagents used in this work were weighed using an electronic analytical balance of Shimadzu AY 220 (Germany) giving a maximum sensitivity of 10^{-4} g and an accuracy of $\pm 0.01\%$. Rare earth elements concentrations were determined by spectrophotometer. The analysis of sulphate was determined spectrophotometer Metertech Inc model Sp-8001, (Germany) with the range 200-1100 nm with a wavelength accuracy of ± 1 nm. One match of 5 cm^3 quartz cell with a pass length of 1cm was used for both samples and blank reagent. Calcium, magnesium, chloride, carbonate and bicarbonate were determined by titration technique [10]. Sodium and potassium were determined by a Sherwood flame photometer model 410 (England), using a series of chemical standard solutions. The atomic absorption "Thermo electronic corporation", S series (England), was applied for some trace elements estimation in samples such as Pb, Mn, Zn, Cu, Cd and Fe. Each element was determined using its corresponding operating parameters (wave length, slit settling and light source).

2.3 Uranium Determination

U was determined fluorometrically by laser fluorometer 'UA-3' [Uranium Analyzer (Scintrex, Canada)] in different solutions. The nitrogen laser pulse rate is 16 times per second and pulse duration is 3–4 ns. The excitation wavelength is 337.1 nm and the wavelength of measurement is 495 nm. Integration time is 4 s. The procedure was as follows: specific sample volume ranged from 10 to 50 μL depending mainly on U concentration on the aqueous solution was mixed with the buffer solution (500 g of $\text{NH}_4\text{H}_2\text{PO}_4$ + 50mL H_3PO_4 in 2 L) by the ratio buffer to sample = 2/3, completed up to 7 mL with distilled water and mixed well. The fluorescence intensity is measured, and the concentration of uranium is calculated from a calibration plot obtained using solutions of known uranium content [11].

2.4 Thorium Determination

Thorium was measured spectrophotometrically by UV-Double Beam Spectrophotometer (UNICAM). The optical system was checked automatically, and the instrument was periodically calibrated. The decomposition procedure for the samples were done as follow: 0.2 g of sample was mixed with 20 ml HF, evaporates till dryness, then diluted with 15 ml HF (1:1), then filtration and treating the precipitate with 10 ml conc. HClO_4 and 5 ml conc HNO_3 and heat till dryness. 15 ml 1:1 HCl were added to the residue and completed to the required volume for analysis.

Then, thorium was extracted from acidic solution using TOPO and analyzed in the stripped solutions using the proposed 1,4-DHA dye as follow: The purplish-blue colored "Th(IV)-(1,4-DHA)" complex was prepared by adding 0.5 ml of 10^{-3} M 1,4-DHA solution to an aliquot of the sample and diluted the volume with methanol and double distilled water (50% methanol) in 10 mL standard measuring flask (the pH of the net solution should be 3.25), finally measuring the absorbance of the complex formed in a 1cm cell against a reagent blank at 600 nm [12].

2.5 Zirconium Determination

To an aliquot portion of sample solution 4 ml of arsenazo III and 37ml concentrated HCl are added then completed up to 50 ml with double distilled water, mixed well and measured at 665nm [13].

3 Results and Discussion

3.1 Hydrochemical Characteristics.

The chemical results of the analyzed water samples indicate the following chemical properties of the studied water samples; they have pH values range around 0.35 (sample 1/2) and 0.84 (sample 2/1) indicating very acidic media (Tables 1 and 2). They are characterized by turbid and colored. The T.D.S varies between 780 ppm (sample 1/1) and 20000 ppm (sample x), (Tables 1 and 2). The hydrochemical characteristics of studied water samples are expressed as hydrochemical percentages and ion ratios. They are arranged in a decreasing order of their concentrations. Among the cationic concentrations, sodium represents the most dominant followed by calcium and magnesium ions ($\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$) in all samples except samples (No. 1/3 and x). Sample (No. 1/3) has sodium represents the most dominant followed by magnesium or calcium, while, $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$ in sample (x). The bicarbonates concentrations are the most dominant anions followed by chloride and sulphates ($\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$), except in samples (No. 1/3 and 3/2) $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$ and $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^-$ in (sample No. x) (Tables 3 and 4).

3.2 Ion Ratios

The hydrochemical ratios of $r\text{Na}^+/r\text{Cl}^-$, $r\text{K}^+/r\text{Cl}^-$, $r\text{Ca}^{2+}/r\text{Cl}^-$, $r\text{Mg}^{2+}/r\text{Cl}^-$, $r\text{SO}_4^{2-}/r\text{Cl}^-$, $r\text{Ca}^{2+}/r\text{Mg}^{2+}$ and $r\text{Cl}^- - r(\text{Na}^+ + \text{K}^+) / r\text{Cl}^-$ in equivalent concentration are useful tools for detecting water contamination or mixing (Tables 3 and 4). The $r\text{Na}^+/r\text{Cl}^-$ ratio expresses the sodium chloride imbalance in water. It is always higher than unity in fresh meteoric water, while it is less than unity in sea water average 0.85 [14].

The ratio of $r\text{Na}^+/r\text{Cl}^-$ has higher value than unity which indicates the contribution with fresh water except samples (No. 1 /2 and x). The ratio $r\text{K}^+/r\text{Cl}^-$ varies between 0.067 and 0.238.

Table 1: Chemical analysis of water samples.

Sample No.	pH	T.D.S (ppm)	Units	Cations				Total cations	Anions				Total anions
				Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺		Cl ⁻	SO ₄ ⁻⁻	CO ₃ ⁻⁻	HCO ₃ ⁻	
1/1	0.52	780	ppm	106.	37.2	80.1	36.48	12.60	141.8	125	120	122	12.60
			epm	95	4	6	3		4	2.6	4	2	
			%	4.65	0.95	4	23.80		31.74	20.63	31.74	15.87	
			epm	36.8	5	31.7							
1/2	0.35	1100	ppm	165	20	110.	66.88	18.68	265.8	142.85	180	122	18.46
			epm	7.17	0.51	22	5.5		7	2.97	6	2	
			%	38.3	2	5.5	29.44		7.49	16.08	32.50	10.83	
			epm	8	2.74	29.4			40.57				
1/3	0.49	1060	ppm	205	26.3	80.1	54.72	18.08	283.6	142.85	165	91.5	17.97
			epm	8.91	8	6	4.5		8	2.97	5.5	1.5	
			%	49.2	0.67	4	24.88		44.51	16.52	30.60	8.34	
			epm	6	6	22.1							
1/4	0.50	1560	ppm	296	35.5	130.	66.88	25.77	354.5	214.28	211.8	233.66	25.35
			epm	12.8	5	26	5.5		10	4.46	3	3.83	
			%	6	0.91	6.5	21.34		39.44	17.59	7.06	15.10	
			epm	49.9	1	25.2					27.85		
1/5	0.64	1165	ppm	238	29.1	80.1	48.64	19.08	265.8	142.85	155	193.16	18.78
			epm	10.3	6	6	4		7	2.97	5.16	3.16	
			%	4	0.74	4	20.96		7.49	15.81	27.47	16.82	
			epm	54.1	7	20.9			39.88				
2/1	0.84	830	ppm	116	21.1	80.1	51.07	13.78	177.2	107.14	124	142.3	13.69
			epm	5.04	1	6	4.2		5	2.23	4.13	2.33	
			%	36.5	0.54	4	30.47		5	16.28	30.16	17.01	
			epm	7	1	29.0			36.52				
2/2	0.70	1170	ppm	185	34.4	120.	60.8	19.92	265.8	133.92	175.6	183	19.18
			epm	8.04	4	24	5		7	2.79	6	3.05	
			%	40.3	0.88	6	25.10		7.49	14.54	5.85	15.90	
			epm	6	4.41	30.1			39.05		30.50		
2/3	0.47	1460	ppm	264	35.5	120.	72.96	24.38	194.97	116.07	330.6	315.16	24.08
			epm	11.4	5	24	6		5.49	2.41	11.02	5.16	
			%	7	0.91	6	24.61		22.79	10.0	45.76	21.42	
			epm	47.0	3.73	24.6							

Table 2: Chemical analysis of water samples.

Sample No.	pH	T.D.S (ppm)	Units	Cations				Total cations	Anions				Total anions
				Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺		Cl ⁻	SO ₄ ⁻⁻	CO ₃ ⁻⁻	HCO ₃ ⁻	
2/4	0.53	1350	ppm	224	29.16	120.	72.96	22.47	301.3	178.5	191.1	223.66	22.24
			epm	9.73	0.74	24	6		2	7	6	3.66	
			%	43.30	3.29	6	26.70		8.49	3.72	6.37	16.45	
			epm			26.7	0		38.17	16.72	28.64		

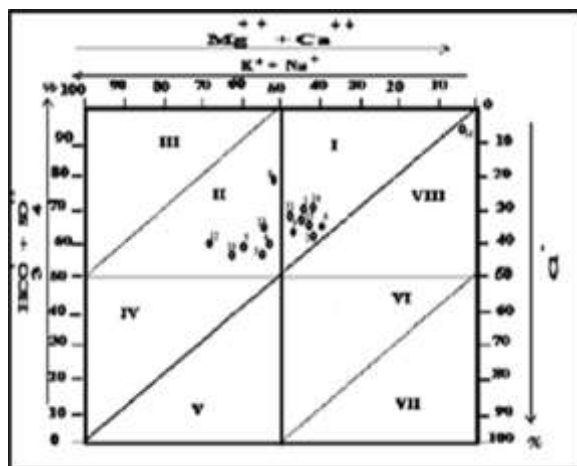


Fig.2: Ovitchinikov's graph for hydrochemical representation of the studied water samples, leaching of black sand.

Note: Sample No. 1 refers to (1/1), 2 (1/2), 3 (1/3), 4 (1/4), 5 (1/5), 6 (2/1), 7 (2/2), 8 (2/3), 9 (2/4), 10 (2/5), 11 (3), 12 (3/2), 13 (3/4), 14 (3/5), 15 (4) and 16 (X).

3.4 Evaluation of Water Samples for Different Uses.

3.4.1. Drinking Water Purposes

The application of the international standards for drinking water [16,17,18] revealed that all water samples are fairly fresh with T.D.S range between 700 -1500 ppm except samples (No. 1/4 , 3/5, 4 and x) . Possible fresh water type with T.D.S range between 1500 and 2000 ppm for water samples (No. 1/4and 3/5). Slightly brackish water type with T.D.S range between 2000-3200 for sample (No. 4). Very salty water type with T.D.S > 10000 ppm for sample (No. x) (Table 5).

3.4.2 Domestic Water Purposes

Water for household purposes must have hardness less than 100 [19]. The hardness (H) is calculated as: Hardness (H) = $(Ca^{++} + Mg^{++}) \times 50$ epm. According to the calculated hardness, all studied water samples are not suitable for household purposes (Table 6).

3.4.3.3 Classification According to Sodium Percentage (Na %).

Water for irrigation must have Na % less than 20 which can be calculated using the equation: $Na \% = (Na^{+} + K^{+} / Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}) \text{ epm} \times 100$. Based on the classification of sodium percentage [19], water sample (No. x) are excellent, but samples (No. 2/5 and 3/2) are bad and all samples are permissible except (x, 2/5 and 3/2) (Table 6).

3.4.4 Livestock and Poultry Purposes.

The evaluation classification for livestock and poultry uses depending on the T.D.S concentrations [23]. It is found that, water samples (No. 1/1, 2/1, 3 and 3/2) are excellent for all classes of livestock and poultry with T.D.S less than 1000 ppm. While, all water samples (No. 1/2, 1/3, 1/4, 1/5, 2/2, 2/3, 2/4, 2/5, 3/4, 3/5 and 4) have T.D.S range between 1000-2999 ppm, are very satisfactory for all classes of livestock and poultry but may cause temporary and mild diarrhea. While, sample (No. x) unfit for poultry and probably for swine, risk in using for pregnant or lactating cows, horses or sheep due to T.D.S more than 5000 ppm.

3.4.5. Evaluation of Water Samples for Industrial Purposes.

Water evaluation for industrial purposes is very important especially in the undeveloped desert area. Some industrial activities are expected to appear due to the growth of the population and movement towards the desert lands around the area of the study. The international standards [24,25] for some industrial projects and by applying the standard limits, all water samples are suitable for petroleum industry except sample (No. x). While, they are unsuitable for textile because T.D.S are higher than (100-200) ppm. Moreover, all water samples are not suitable for paper industry because T.D.S are higher than (200-500) ppm.

3.4.6 Evaluation of Water Samples for Building Purposes

The high sulphate ion concentration can greatly affect the quality of concrete. When sulphate exceeds 300 ppm, it reacts with cement and form gypsum. The only treatment for high sulphate in water is by using iron cement to make dense concrete. All water samples are suitable for building because SO_4^{2-} is lower than 300 ppm except sample (No. x) [26].

3.5 Trace Elements.

Trace elements have special interest and considerable importance in the study of the water pollution. Trace elements found in water are a mirror of that found in the surrounded rocks which are leached by the movement of water and also controlled by the mineralogical changes which take place during alteration and nature of fluid. The concentration of the analyzed trace elements of the studied water samples are presented in table (7), and compared to the maximum permissible concentrations in drinking and irrigation purposes. The maximum permissible limits for trace metals concentration of these elements were detected for drinking and irrigation by the different organizations

Table 3: Hydrochemical formula, hypothetical salt combination (%) and hydrochemical ratios for studied water samples.

Sample No.	Hydrochemical formula	Hypothetical salt combination (%)	Hydrochemical ratios						
			rNa ⁺ /rCl ⁻	rK ⁺ /rCl ⁻	rCa ⁺⁺ /rCl ⁻	rMg ⁺⁺ /rCl ⁻	rSO ₄ ⁻² /rCl ⁻	rCa ⁺⁺ /rMg ⁺⁺	rCl ⁻ /r(Na ⁺ +K ⁺)/rCl ⁻
1/1	HCO ₃ 47.61, Cl 31.74, SO ₄ 20.63,	NaCl (13.74), Ca (HCO ₃) ₂ (31.73), Mg (HCO ₃) ₂ (15.89), Na ₂ SO ₄ (12.72), MgSO ₄ (7.91).	1.16	0.2	0.99	0.74	0.64	1.33	-0.40
	Na 44.46, Ca 31.73, Mg 23.80		6	38	9	9	9		
1/2	HCO ₃ 43.33, Cl 40.57, SO ₄ 16.08,	NaCl (40.57), Ca (HCO ₃) ₂ (29.44), MgSO ₄ (15.33), Mg (HCO ₃) ₂ (13.91), MgSO ₄ (0.55).	0.94	0.0	0.72	0.72	0.39	1.0	-0.013
	Na 41.12, Ca 29.44, Mg 29.44		6	67	5	5	6		
1/3	Cl 44.51, HCO ₃ 38.94, SO ₄ 16.52,	NaCl (44.51), Ca (HCO ₃) ₂ (22.11), Mg (HCO ₃) ₂ (16.84), Na ₂ SO ₄ (8.48), MgSO ₄ (8.04).	1.10	0.0	0.49	0.55	0.37	0.88	-0.190
	Na 52.99, Mg 24.88, Ca 22.11		6	83	6	8	1	8	
1/4	HCO ₃ 42.95, Cl 39.44, SO ₄ 17.59,	NaCl (39.44), Ca (HCO ₃) ₂ (25.22), Mg (HCO ₃) ₂ (17.74), Na ₂ SO ₄ (13.99), MgSO ₄ (3.6).	1.26	0.0	0.63	0.54	0.44	1.18	-0.354
	Na 53.43, Ca 25.22, Mg 21.34		89	9	1	5			
1/5	HCO ₃ 44.29, Cl 39.88, SO ₄ 15.81,	NaCl (39.88), Ca (HCO ₃) ₂ (20.96), Mg (HCO ₃) ₂ (20.96), Na ₂ SO ₄ (15.81), NaHCO ₃ (2.41).	1.35	0.0	0.52	0.52	0.39	1.0	-0.456
	Na 58.10, Ca 20.96, Mg 20.96		98	5	5	6			
2/1	HCO ₃ 47.17, Cl 36.52, SO ₄ 16.28,	NaCl (36.52), Ca (HCO ₃) ₂ (29.02), Mg (HCO ₃) ₂ (18.16), MgSO ₄ (12.31), Na ₂ SO ₄ (3.97).	1.00	0.1	0.79	0.83	0.44	0.95	-0.108
	Na 40.49, Mg 30.47, Ca 29.02		1	07	4	4	5	2	
2/2	HCO ₃ 46.40, Cl 39.05, SO ₄ 14.54,	NaCl (39.05), Ca (HCO ₃) ₂ (30.12), Mg (HCO ₃) ₂ (16.28), MgSO ₄ (8.82), Na ₂ SO ₄ (5.72).	1.03	0.1	0.77	0.64	0.37	1.2	-0.146
	Na 44.77, Ca 30.12, Mg 25.10		3	12	1	2	2		
2/3	HCO ₃ 67.18, Cl 22.79, SO ₄ 10.00,	Ca (HCO ₃) ₂ (24.61), Mg (HCO ₃) ₂ (24.61), NaCl (22.79), Na HCO ₃ (17.98), Na ₂ SO ₄ (10.0).	2.06	0.1	1.07	1.07	0.43	1.0	-0.122
				63			8		

3.5.1 Cadmium

The cadmium (Cd) is a relative rare metal, and considered as one of the most toxic metals pollutants in surface water. Chemically Cd is very similar to zinc and both metals frequently undergo geochemical processes together. The permissible value of Cd for drinking water is 3 ppb [30], while the limited permissible of Cd for drinking water does not exceed 5 ppb [31] The permissible value of Cd for drinking water is 10 ppb [25, 27, 28]. Accordingly, all water washing samples are lower than the limited permissible values for both drinking and irrigation purposes (Table 7).

3.5.2. Lead

The lead (pb) is belonging to the most dangerous heavy metal pollutants in surface water which represents an exchangeable ion for calcium and potassium. The increase in Pb content in water is due to leaching of lead bearing minerals as a result of weathering. The concentration of Pb in studied water samples ranging between 0.0178 ppb(sample No. 4) and 2.7183 ppb of (sample No. 1/4). The recommended guideline value for drinking water is 50 ppb [28, 29, 31], while the maximum concentration level is 10 ppb [30]. All water samples are under the safe limit and

Table 4: Hydrochemical formula, hypothetical salt combination (%) and hydrochemical ratios for studied water samples.

Sample No.	Hydrochemical formula	Hypothetical salt combination (%)	Hydrochemical ratios						
			r_{Na^+}/r_{Cl^-}	r_{K^+}/r_{Cl^-}	$r_{Ca^{++}}/r_{Cl^-}$	$r_{Mg^{++}}/r_{Cl^-}$	$r_{SO_4^{--}}/r_{Cl^-}$	$r_{Ca^{++}}/r_{Mg^{++}}$	$r_{Cl^-} / r_{(Na^++K^+)/r_{Ca^{++}}}$
2/4	HCO ₃ 45.09, Cl 38.17, SO ₄ 16.72,	NaCl (38.17), Ca (HCO ₃) ₂ (26.70), Mg (HCO ₃) ₂ (18.4), Na ₂ SO ₄ (8.42), MgSO ₄ (8.3)	1.13	0.08	0.69	0.69	0.438	1.0	-0.220
	Na 46.59, Ca 26.70, Mg 26.70								
2/5	HCO ₃ 44.06, Cl 43.09, SO ₄ 12.83,	NaCl (43.09), Ca (HCO ₃) ₂ (19.98), Mg (HCO ₃) ₂ (17.12), Na ₂ SO ₄ (12.83), NaHCO ₃ (6.96).	1.36	0.08	0.46	0.39	0.297	1.16	-0.459
	Na 62.88, Ca 19.98, Mg 17.12								
3	HCO ₃ 50.82, Cl 33.17, SO ₄ 15.99,	NaCl (33.17), Ca (HCO ₃) ₂ (29.62), Mg (HCO ₃) ₂ (21.2), Na ₂ SO ₄ (15.8), MgSO ₄ (0.19).	1.33	0.14	0.89	0.64	0.482	1.38	-0.476
	Na 48.97, Ca 29.62, Mg 21.39								
3/2	Cl 42.31, HCO ₃ 40.68, SO ₄ 16.99,	NaCl (42.31), Ca (HCO ₃) ₂ (17.61), Na ₂ SO ₄ (16.99), Mg (HCO ₃) ₂ (14.09), Na HCO ₃ (8.98).	1.48	0.12	0.41	0.33	0.401	1.24	-0.613
	Na 68.28, Ca 17.61, Mg 14.09								
3/4	HCO ₃ 54.33, Cl 35.18, SO ₄ 10.47,	NaCl (35.18), Mg (HCO ₃) ₂ (23.23), Ca (HCO ₃) ₂ (23.23), Na ₂ SO ₄ (10.47), NaHCO ₃ (7.87).	1.42	0.09	0.66	0.66	0.297	1.0	-0.521
	Na 53.52, Ca 23.23, Mg 23.23								
3/5	HCO ₃ 62.25, Cl 28.55, SO ₄ 9.18,	Ca (HCO ₃) ₂ (30.08), NaCl (28.55), Mg (HCO ₃) ₂ (26.32), Na ₂ SO ₄ (9.18), NaHCO ₃ (5.85).	1.37	0.15	1.05	0.92	0.321	1.14	-0.526
	Na 43.58, Ca 30.08, Mg 26.32								
4	HCO ₃ 56.55, Cl 33.87, SO ₄ 9.56,	Ca (HCO ₃) ₂ (37.57), NaCl (33.87), Mg (HCO ₃) ₂ (16.10), Na ₂ SO ₄ (9.56), NaHCO ₃ (2.88).	1.27	0.09	1.10	0.47	0.282	2.33	-0.367
	Na 46.31, Ca 37.57, Mg 16.10								
X	SO ₄ 71.87, HCO ₃ 20.9, Cl 7.21,	MgSO ₄ (42.8), CaSO ₄ (29.07), Ca (HCO ₃) ₂ (20.9), NaCl (6.44), MgCl ₂ (0.77).	0.660	0.23	6.93	6.04	9.96	1.14	0.106
	Ca 49.97, Mg 43.57, Na 6.44								

suitable for drinking according to the standard limits [28, 29, 30, 31]. The maximum recommended concentration of lead in irrigation water is 5000 ppb [22], accordingly all the studied water samples contain lead much lower than this recommended guide line value.

3.5.3. Copper

The copper (Cu) is an essential element for human body and plant metabolism. Cu concentration in all studied water samples seems to be much lower than the limited permissible values for both drinking and irrigation purposes. Where the guideline value for copper in drinking water is 1000 ppb [16, 28], while the guideline value for copper in irrigation water is 2000 ppb [22] and 200 ppb [25].

3.5.4 Manganese.

The manganese (Mn) is an essential element for both plants and animals' life forms. The guideline value for Mn in drinking water is 100-500 ppb [16]. Mn content in the studied water samples ranging between 0.35 ppb (sample No. 2/3) and 160.88 ppb (sample No. X). Therefore, all water samples are suitable for drinking purposes. For irrigation the maximum recommended concentration of Mn^{2+} is 200 ppb [22], therefore all studied water samples are suitable for irrigation (Table 7).

3.5.5. Zinc

The zinc (Zn) plays an essential role in human metabolism, the total content of Zn in the earth's crust is 200 ppm by weight. The guide line value of Zn permissible in drinking water is 3000 ppb [30]. In Egypt, Zn concentration in drinking water is accepted as the permissible limit 5000 ppb [29]. For irrigation water, the permissible limits ranging

between 2000 and 10000 ppb [16]. The concentration of Zn in the water samples ranges between 0.064 ppb (sample 3/4) and 1.517 ppb (sample No. 4). Accordingly, all the studied water samples are lower than the limited permissible values for both drinking and irrigation purposes. The dosages of ZrO_2 in the range of 100–350 mg/kg are safe for clinical use [32]. Although the results indicates involvement of oxidative damage in the liver and serum caused by ZrO_2 at high dose (Table 7).

3.5.6 Iron

Iron (Fe) is considered as contaminants under guidelines for public water supplies [28], which causes offensive taste, odor, color, corrosion, staining but have no direct effective health. Iron concentration in studied water samples ranging between 78190 ppb (sample No. 1/1) and 6255200 ppb (sample No. X), all water samples are unsuitable for drinking and contain iron value higher than the recommended guideline value 300 ppb [28]. All water samples are unsuitable for irrigation purposes, where they are higher than the guideline for iron concentration in irrigation water (5000 ppb) according to [22].

3.5.7 Uranium

Uranium has two oxidation states, tetravalent and hexavalent, under reducing condition, uranium may occur as U^{4+} ions, which are soluble in water of low pH. The water samples are considered as a transportation medium of dissolved uranium from the source rock to the deposition area. The behavior of uranium in the water samples is affected by many factors such as: depth of aquifer and depth to ground water surface, climate, rate of evaporation processes and geological setting of the aquifer. The uranium content in the surface and subsurface water is affected by many factors such as: depth of aquifer and depth to ground water surface, climate, rate of evaporation

Table 5: Characteristic features of water samples and surfacial water based on standard guideline [16,18].

Sample No.	T.D.S (ppm)	Evaluation of samples based on [17].			
		T.D.S. (ppm)	Quality	Type	Sample No.
1/1	780	< 500	Good potable	Fresh water	-----
1/2	1100	500-700	Fresh		-----
1/3	1060	>700-1500	Fairly fresh		1/1, 1/2 , 1/3, 1/5, 2/1, 2/2, 2/3, 2/4, 2/5, 3, 3/2 and 3/4
1/4	1560				1/4 and 3/5
1/5	1165	>1500-2000	Possible fresh	Brackish	4
2/1	830	>2000-3200	Slightly brackish		-----
2/2	1170				-----
2/3	1460	>3200-4000	Brackish		-----
2/4	1350	>4000-5000	Definitely brackish		-----
2/5	1060			-----	

3	920	>5000-6000	Slightly salty	Saline water	-----
3/2	890				-----
3/4	1290	>6000-7000	Salty		-----
3/5	1600				-----
4	2320	>7000-10000	Very salty		-----
X	20000	>10000	Very salty	x	

Table 6: Hardness, Na% and sodium adsorption ratio (SAR) of the studied water samples and surfacial water.

Sample No.	*Hardness (H)	**SAR	***Na, (%)	SAR standard ranges and grades classified according to SAR and [19]		Na% standard ranges and grades classified according to SAR and [19]	
				SAR range	Grade	Na% range	Grade
1/1	350	2.48	44.46	< 10	Excellent	< 20	Excellent
1/2	550	3.05	41.12				
1/3	425	4.32	53.0				
1/4	600	5.25	53.43				
1/5	400	5.17	58.10				
2/1	410	2.48	40.49	10-18	Good	20-40	Good
2/2	550	3.42	44.77				
2/3	600	4.68	50.77				
2/4	600	3.97	46.59				
2/5	325	5.73	62.89				
3	387.5	3.41	48.97	18-26	Fair	>60-80	Bad
3/2	225	5.94	68.28				
3/4	500	4.82	53.53				
3/5	750	3.80	43.58				
4	1000	5.07	46.32				
X	14600	1.22	6.44	>26	Poor	>80	Unsuitable for irrigation

$$\text{Hardness (H)} = (\text{Ca}^{++} + \text{Mg}^{++}) \times 50 \text{ epm}, \text{ SAR} = \frac{\text{Na}}{\sqrt{\text{Ca} + \text{Mg}/2}} \text{ (epm)}, \text{ Na \%} = (\text{Na}^+ + \text{K}^+ / \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+) \times 100 \text{ epm}$$

Table 7: Trace elements analyses for the studied water samples (ppb).

Sample No.	Mn	Fe	Zn	Cu	Cd	Pb	Zr
1/1	0.58	78190	0.17	0.046	0.014	N.D	15000
1/2	1.022	156380	0.12	0.017	0.007	N.D	16200
1/3	0.611	234570	0.194	0.027	N.D	N.D	15000
1/4	1.8	273665	0.23	0.059	N.D	2.7183	14800
1/5	2.68	312760	0.467	0.035	0.0011	N.D	15100
2/1	1.138	344036	0.128	0.0411	N.D	N.D	15400
2/2	2.75	625520	0.326	0.0184	N.D	N.D	15800
2/3	0.35	781900	0.268	0.0155	N.D	N.D	16700
2/4	1.51	938280	0.234	0.041	0.0011	N.D	16500
2/5	1.37	1251040	0.18	0.081	N.D	N.D	18000
3	1.269	2502080	0.158	0.0584	N.D	N.D	25000
3/2	1.51	3127600	0.21	0.024	N.D	N.D	22000
3/4	0.62	3909500	0.064	N.D	N.D	N.D	20000
3/5	0.92	4691400	0.222	0.0133	N.D	N.D	20500
4	3.56	5473300	1.517	0.1172	N.D	0.0178	20000
X	160.88	6255200	0.359	13.1	1.014	N.D	10000

Organization	Permissible limits for drinking						
[27]					10 ppb		
[25]					10 ppb		
[28]		300 ppb		1000 ppb	10 ppb	50 ppb	
[16]	100-500ppb			1000 ppb			
[30]			3000ppb		3ppb	10ppb	
[29]			5000 ppb			50 ppb	
[31]					5ppb	50 ppb	
Organizations	Permissible limits for irrigation						
[25]				200 ppb			
[16]			2000 - 10000 ppb				
[22]	200 ppb	5000 ppb		2000 ppb		5000 ppb	

processes and geological setting of the aquifer. The uranium content in the surface and subsurface water is changing greatly depending on the type of pH, Eh and the deposited types of the lithofacies.

3.5.7.1 Effect of Uranium on Health

Uranium is considered as a toxic and radioactive element for human, the chemical toxicity of uranium is due to its combination in the hexavalent state with phosphate group on the cell's surface in human body, hence blocking normal metabolic processes necessary for cell's survival. Hexavalent uranium injures the kidneys preventing normal waste product elimination such as urea; some people who drink water containing alpha emitter in excess of the maximum contamination levels over many years may have an increased risk of getting cancer. Uranium concentrations (Table 8) in the studied water samples ranged between 848 and 13764 with 31604.17 mBq/l as an average. The maximum permissible limits for trace metals concentration of uranium were detected for drinking and irrigation by the different organizations [16, 3, 25, 31], (Table 8). The studied water samples resulted from washing of black sand during different stages of processing are very high, especially in the final stages in comparison with the permissible guidelines, suggesting their severe effect on the surrounding surficial and underground water leading their contamination and consequently their hazards.

In Finland, for example, some waters have shown activities above 1.5 Bq /l in uranium, which is due to high uranium concentration in the subterranean rocks [33]. Uranium concentrations in groundwater samples from southwestern Sinai reach up to 25,413 mBq/l [34]. The international guideline value according to [3] was about 30 ppb (372 mBq/l). These high values of uranium concentrations groundwater [35]. Very high uranium concentrations in the studied water washing samples were inherited from water-black sand interaction, especially in the late stages of

washing due to acidity arising and increasing the dissolution of the metamict minerals like zircon.

3.5.8. Thorium

Thorium is a radioactive element that has only one single isotope Th-232. Thorium content is about four times greater than uranium in the earth crust, the major salts of Th are insoluble or weakly soluble in water, accordingly its constituents in natural waters are much less than that of uranium. Egyptian data about thorium in water are completely limited in literature in addition to scarcity of available worldwide published values about thorium concentration in waters. It is 0.4 mBq /L for river water, 0.8±0.08 mBq / L for hot springs water and 0.037-0.05 mBq /L for tap water, [36] and (< 0.1 ppb) for drinking water [37]. Thorium in ground water of CentraEasternDesert, Egypt, is between 0.7 and 6.65 ppb [38]. While in ground water of Wadi Nasib, West Central Sinai ranged between 2.5 and 9.2 ppb [39]. The studied water washing samples range between 82000 and 150000 ppb except samples No. (2/2, 2/5, 3, 3/4 and 4) are under limit of detection (Table 9).

Table 8: Uranium analyses for the studied water samples (ppb) from black sands processing.

Sample No.	U (ppb)	U (mBq/l)
1/1	70	868
1/2	153	1897
1/3	194	2406
1/4	225	2790
1/5	300	3720
2/1	345	4278
2/2	540	6696
2/3	720	8928
2/4	860	10664
2/5	1000	12400
3	2000	24800
3/2	3000	37200

3/4	4000	49600
3/5	5000	62000
4	5200	64480
X	11100	137640
Min.	70	868
Max.	11100	137640
Av.	2548.72	31604.17
Organizations	Permissible limits for drinking water (ppb)	Permissible limits for drinking water (mBq/l)
[16]	120	1488
[3]	30	372
[25]	35	434
[31]	9	111.6

Table 9: Thorium and total rare earth elements (TREES).

Sample No.	Th (ppb)	TREES (ppb)
1/1	82000	4360
1/2	85000	4210
1/3	90000	4410
1/4	115000	5130
1/5	118000	5260
2/1	110000	4450
2/2	N.D	4800
2/3	130000	4820
2/4	125000	4310
2/5	N.D	5010
3	N.D	4060
3/2	134000	N.D
3/4	N.D	N.D
3/5	150000	N.D
4	N.D	5820
X	144000	44700

3.6 REEs Analyses

Mining and processing of rare earth ore is recorded to be of environmental impacts, essentially causing atmospheric pollution, acidic wastewater, and radioactive tailings [40, 41]. However, significant REE enrichment in water, soil and vegetation near mining sites in China led to environmental impacts of REEs [42, 43]. Rivers near the mining sites of rare earths in China, have dissolved REE concentrations three orders of magnitude higher than unperturbed rivers [44].

REEs are widely used in plant fertilizers and feed additions for farm animals in many countries, showing positive physiological effects [45]. However, recent laboratory studies illustrate the potential for both bioaccumulation and toxicity of REEs in fish and humans [46, 47]. It is indicated in certain study that the maximum REEs permissible

concentrations range from 1.8 to 22 mg L⁻¹ in fresh surface waters and from 1.8 to 18.8 g kg⁻¹ d.w. in lake sediments [48]. The studied water washing samples range between 4060 and 44700 ppb (Table 9) indicating out of range values suggesting their hazards on any type of water whether surficial or underground water [48].

4 Conclusions

Among the cationic concentrations, sodium represents the most dominant followed by calcium and magnesium ions (Na⁺ > Ca²⁺ > Mg²⁺) in all samples except samples (No. 1/3 and x). Sample (No. 1/3) has sodium represents the most dominant followed by magnesium or calcium, while, Ca²⁺ > Mg²⁺ > Na⁺ in sample (x). The bicarbonates concentrations are the most dominant anions followed by chloride and sulphates (HCO₃⁻ > Cl⁻ > SO₄²⁻), except in sample (No. 1/3) Cl⁻ > HCO₃⁻ > SO₄²⁻ while, Cl⁻ > HCO₃⁻ > SO₄²⁻ in (sample 3/2) and SO₄²⁻ > HCO₃⁻ > Cl⁻ in (sample No. x). Water sample (No. X) characterized by low chloride and bicarbonate water indicating marine origin water type, while the water samples (No. 1/1, 1/2, 2/1, 2/2, 2/4, 3, 3/5 and 4) are characterized by high Ca⁺⁺ and Mg⁺⁺ and high bicarbonate, indicating meteoric origin water type. On the other hand, the water samples (No. 1/3, 1/4, 1/5, 2/3, 2/5, 3/2 and 3/4) have high bicarbonate and high Na⁺ and K⁺, indicating meteoric origin water type. All water samples are fairly fresh with T.D.S range between 700 -1500 ppm except samples (No. 1/4, 3/5, 4 and x).

Possible fresh water type with T.D.S range between 1500 and 2000 ppm for water samples (No. 1/4 and 3/5). Slightly brackish water type with T.D.S range between 2000-3200 for sample (No. 4). Very salty water type with T.D.S > 10000 ppm for sample (No. X). Low Salinity the studied water samples gave it the suitability for irrigation, with the exception of sample (X) which isn't suitable for irrigation. All water samples are suitable for petroleum industry except sample (No. X), but are unsuitable for textile and paper industry because T.D.S are higher than (200-500) ppm. Also, all water samples are suitable for building because SO₄²⁻ is lower than 300 ppm except sample (No. x). The concentration of trace elements Mn, Zn, Cu, Cd and Pb illustrate that the studied washing water samples have permissible concentration suitable for drinking, laundry, irrigation, building, industrial, livestock and poultry except (Fe and Zr) elements. All water samples are unsuitable for drinking and irrigation contain iron and zirconium value higher than the recommended guideline values. Uranium, thorium and rare earths have values higher than the maximum permissible limits supported by organizations and recent studies indicating unsuitable limits for drinking water and other uses, in addition to their hazard on surficial, underground water and the surrounding plants.

Recommendations

As a result of water-black sand interaction during the

physical upgrading processes of black sand for various purposes. The resultant grey or black water quality and its suitability for irrigation and domestic purpose were examined by various hydrochemical parameters. The resulting water contains greater concentrations of uranium and rare earth elements than acceptable limits, that reflecting its great hazards. It is recommended to dispose the water of processing by recycling and treatment in order to extract the high concentrations of uranium, thorium and REEs by applying advanced adsorption techniques.

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