

Characterization of phosphogypsum wastes associated with phosphoric acid and fertilizers production

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ABSTRACT

The present work is directed to characterize the phosphogypsum (PG) wastes associated with phosphoric acid produced by the wet process in industrial facility for the production of fertilizers and chemicals in Egypt. The PG waste samples were characterized in terms of spectroscopic analysis (X-ray diffraction, X-ray fluorescence, IR spectra) and radiometric analysis (γ - and α -measurements). The γ -ray measurements showed that the average activity concentrations are 140 ± 12.6 , 459 ± 36.7 , 323 ± 28.4 , 8.3 ± 0.76 and 64.3 ± 4.1 Bq/kg for U-238, Ra-226, Pb-210, Th-232 and K-40, respectively. The α -particle measurements of uranium isotopes showed that the average activity concentrations of U-238, U-235 and U-234 were 153 ± 9.8 , 7 ± 0.38 , 152 ± 10.4 Bq/kg, respectively. The average radiochemical recovery (%) of the destructive α -particle measurements is $\sim 70\%$ with a resolution (FWHM) of ~ 30 keV. Activity ratios of U-238/Ra-226 and U-238/Pb-210 were less than unity (i.e., <1) and equal to 0.31 ± 0.02 and 0.47 ± 0.16 , respectively. The isotopic ratios of U-238/U-235 and U-238/U-234 (in PG and PR samples) were close to the normal values of ~ 21.7 and ~ 1 , respectively and are not affected by the wet processing of phosphate rock (PR). The obtained results of PG waste samples were compared with phosphate rock (PR) samples. The radiation hazard indices are namely, radium activity index ($Ra-Eq > 370$ Bq/kg), total absorbed gamma dose rate ($D_{\gamma T} > 5$ nGy/h) and radon emanation fraction ($Rn-EF > 20\%$). Uncertainty of the sample counting was 95% confidence level of σ . The results indicated the necessity to find suitable routes to decrease and/or redistribute the radionuclide of environmental interest (i.e., Ra-226) in PG wastes, consequently to reduce its radiation impacts in the surrounding environment.

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1. Introduction

The naturally occurring radioactive materials (NORM) are found everywhere. We are exposed to it every day. NORM represent an integral part of the planet, our bodies, the food we eat, the air we breathe, the places where we live and work, and within products we use. Processing of some natural resources concentrates the naturally occurring radionuclides to a degree that they may pose risks to humans and the environment. Therefore, concentration of radionuclides such as uranium (U) and/or thorium (Th) series and their respective decay products in the by-products produced from several industries is technologically enhanced. These by-products are named as: Technically Enhanced – Naturally Occurring Radioactive Materials (TE-NORM). The majority of radionuclides in TE-NORM are found in the U-238 and Th-232 decay chains.

Radium-226 and its decay products (e.g., radon – Rn-222) are quite often used to characterize the redistribution of TE-NORM that result from human activities (Egidi and Hull, 1999).

Phosphoric acid (PA) produced from phosphate rocks by the wet process using sulphuric acid attack accounts for over 90% of its production (Becker, 1989). Accordingly, the solid wastes produced as a by-product, phosphogypsum from these processes increase and accumulate worldwide. Phosphogypsum (PG) is composed mainly of gypsum ($CaSO_4 \cdot 2H_2O$) and contains some impurities of environmental concern such as fluorides (F^-), trace elements (e.g., Fe, Mn, Pb, Cd, etc.) and naturally occurring radioactive materials (NORM), which originate from the phosphate rocks used in this processing. Ra-226 presents the major source of radioactivity in PG wastes produced from sedimentary phosphate rocks (Rutherford et al., 1994). Radioactivity present in PG can enter the environment and may pose radiation exposure concerns through several pathways (Rutherford et al., 1994; Berish, 1990; Carmichael, 1988; Ryzdyski, 1990; Hussain, 1994).

This work is directed to characterize the solid PG waste accompanying phosphoric acid production by the wet process. The

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investigation of PG wastes was carried out based on spectroscopic (XRF, XRD and IR) and radiometric (γ - and α -techniques) measurements. The measurements were used to determine the mineralogy structure, activity concentrations of the different radionuclides (i.e., Ra-226 and Pb-210) in the PG waste samples. Also, activity ratios of parent/daughter radionuclides and some radiation hazard indices were calculated and evaluated.

2. Experimental

2.1. Sampling

The phosphogypsum (PG) waste samples used in this study were collected from industrial facility for phosphoric acid production in January 2004, in Egypt. Number of PG samples was 12 and taken from the PG storage accumulated around the factory using a stainless steel template of dimension $25 \times 25 \text{ cm}^2$ with a thickness of 0.5 cm (5 mm). The solid PG waste sample was screened in atmospheric air for sufficient period (~two weeks) at room temperature (25–30 °C). Then samples were also dried in electric furnace at 110 °C for 2 h to acquire a constant weight to eliminate humidity content. The dried PG waste samples were pulverized, homogenized and sieved using an automatic vibratory sieve (Fritsch analysette 3PRO, Germany) to homogenized particle sizes $\leq 2 \text{ mm}$, while the unhomogenized portion ($>2 \text{ mm}$) was discarded. The sieving recovery (%) was 91.3, 8.5 and 0.2% for the homogenized portion ($\leq 0.6 \text{ mm}$), unhomogenized portion ($>0.6 \text{ mm}$) and loss as dust released into atmosphere, respectively, during the sieving of PG. Also, five samples of the phosphate rocks (PR) used for phosphoric acid production by the wet process were used for the radiometric investigations as well as comparisons with PG waste samples.

2.2. Mineralogical characterization

The main phase composition determination of samples has been carried out using a powder X-ray diffractometer (model XD1180, Schimadzu, Japan) equipped with a copper target and a nickel filter. The micro- and trace elemental analyses of samples have been performed by X-ray fluorescence (XRF) using Philips PW-2400 sequential X-ray spectrometer (Japan). The samples were ground as fine as possible in a laboratory mill. The resulting powder was pressed into pellets of 40 mm diameter and 5 mm thickness, to determine the main and trace elements in the samples. The infrared (IR) spectra of the samples under study were obtained using FT-IR spectrometer (Bomen, Hartman & Braun, and model MB-157, Canada). The samples were ground into fine particles and dried to eliminate the moisture content. Then, certain amount of sample (0.002 g) was mixed with 0.098 g of potassium bromide (KBr). The mixture was compressed into a disc of 5 mm diameter with 1 mm thickness. The IR spectra of the prepared disc were measured and recorded.

2.3. Nuclear spectroscopic measurements

The different radionuclides present in PG waste samples are identified and quantified using HPGe detector (2201-Oxford, TN Nucleus, Oak Ridge, USA) with relative efficiency of 30% and resolution (FWHM) of 1.95 keV at 1.332 MeV for Co-60. The acquisition data of spectra was processed by 8 k MCA and Genie 2000 software (MCA with 8192-channel is connected with IBM personal computer). Energy calibration was performed using several certified sealed point sources of known γ -energy lines, namely, Na-22, Co-60, Ba-133 and Cs-137 (Amersham, England). The efficiency as a function of the γ -energy (in keV) for the used HPGe detector was determined using reference materials (IAEA 312, 313 and 314) with known activity concentrations provided by the Analytical Quality Control Services (AQCS), International Atomic Energy Agency (IAEA), Vienna, Austria (Strachnov et al., 1991a,b,c). An accurate 50 g of the homogenous PG samples was stored in plastic container for radiometric measurements. Activity concentrations of Ra-226 and Pb-210 (of uranium-series) content in the PG waste samples are determined from the measured net count rate (c/s) of 186.2 keV (yield per decay of 3.3%) and 46.2 keV (4%), respectively. Activity concentration of thorium as Th-232 is determined from γ -emissions of its daughters Pb-212 and Ac-228 at 238.6 keV (45%) and 911.1 keV (29%), respectively. Potassium (K-40) is determined at 1461 keV (10.7%). The samples were counted for 2 h. The minimum detectable activity (MDA) was calculated according to Currie (1968) equation. The MDA values for Ra-226 and Th-232 were 1.2 and 1.0 Bq/kg, respectively.

Suitable amounts (150–200 mg) of the PG waste samples and reference materials (IAEA 326 and 327 for quality assurance and quality control) were dried, homogenized and ground to fine particles less than 100 μm . The PG, reference materials and blank samples in pre-cleaned Teflon beakers, are spiked by U-232 (provided by Amersham, England) and digested using concentrated acidic mixture solution ($\text{HNO}_3/\text{HF}/\text{HCl}/\text{H}_3\text{BO}_3/\text{H}_2\text{O}_2$) on sand bath ($\sim 85 \pm 2^\circ\text{C}$). Uranium in samples is separated by solvent extraction (TOPO/cyclohexane), back-solvent extraction ($\text{NH}_4\text{F}/\text{HCl}$), oxidation–reduction ($\text{Ti}^{3+}/\text{HCl}$) into U(IV) and precipitated as $\text{LaF}_3(\text{U})$. Uranium is also purified from the possible interferences (e.g., Th, Ra, Pb, Fe, Ti, etc.) using an anion exchanger (Dowex 1×2 , 50–100 mesh, Cl^- form) and electrodeposited onto

stainless steel disc (Pimpl et al., 1992). The prepared thin final source of uranium is measured using a low background passivated implanted planner silicon (PIPS) α -detector (EG & G ORTEC, TN, USA). The alpha spectra and data were obtained from Maestro-32 emulator. The energy and counting efficiency of the alpha particle spectrometer system were obtained using Am-241 provided by Amersham, England. The whole preparation steps of uranium source from samples are presented in Fig. 1. The minimum detectable activity (MDA) of the α -measurements according to Currie's (1968) formula was $\sim 1 \text{ Bq/kg}$ for U-238, U-235 and U-234.

Uncertainties of the results arise due to a number of factors like volume of samples, efficiency calibrations, peak area determination and random uncertainties associated with background and sample counts. Each sample was measured three times. The combined uncertainties of all these factors did not exceed 7% for Ra-226 and Th-232. For quality assurance and control (QA/QC), reference materials (AQCS/IAEA 312, 313, 314, 326 and 327) were used for efficiency calibration purposes, while sealed point sources were used for energy calibration. In case of alpha measurements, Am-241 source was used for energy and efficiency calibration purposes. Results of the reference materials were good and in agreement with their certified values within errors not exceeding 10%.

2.4. Radiation hazard indices

To represent the activity concentrations of Ra-226, Th-232 and K-40 by a single quantity, which takes into account the radiation hazards associated with them, common radiological indices include radium equivalent (Ra-Eq) activity, absorbed dose rates ($D_{\gamma\text{r}}$) and emanation fraction (Rn-EF). The radium equivalent (Ra-Eq) activity is mathematically calculated according to Beretka and Mathew (1985):

$$\text{Ra-eq (Bq/kg)} = C_{\text{Ra}} + 1.43C_{\text{Th}} + 0.077C_{\text{K}} \quad (1)$$

The absorbed dose rates ($D_{\gamma\text{r}}$) due to γ -radiations in air at 1 m above the ground surface for the uniform distribution of the naturally occurring radionuclides (Ra-226, Th-232 and K-40) were calculated based on guidelines provided by UNSCEAR (1993). The conversion factors used to compute the absorbed γ dose rate ($D_{\gamma\text{r}}$) in air per unit of activity concentration in Bq/kg correspond to 0.462, 0.621 and 0.0417 nGy/h for radium (Ra-226, of U-series), thorium (Th-232) and potassium (K-40), respectively. Therefore, $D_{\gamma\text{r}}$ was calculated according to UNSCEAR (2000):

$$D_{\gamma\text{r}}(\text{nGy/h}) = 0.462C_{\text{Ra}} + 0.621C_{\text{Th}} + 0.0417C_{\text{K}} \quad (2)$$

where C_{Ra} , C_{Th} and C_{K} represent the activity concentrations (Bq/kg) of Ra-226, Th-232 and K-40, respectively.

Amount of radon (Rn-222) gas decayed from its parent (i.e. radium-226), which was released from surface of PG wastes is called 'radon emanation fraction, Rn-EF'. This amount is released into the atmosphere. Determination of Rn-EF was done based on two measurements. In this concern, an accurate 50 g of PG waste samples was mixed with 1 g of an activated carbon. The mixtures were homogenized well, packed in cylindrical cans (250 cm^3), and closed tightly using metallic welding. Then, the prepared samples were initially counted for 100 min after sealing the metallic cans. After the first measurements, the samples were kept at low temperature to attain the radioactive equilibrium between radon-222 and its short-lived decay daughters, i.e., Bi-214 and Pb-214. After about 30 days, the samples were counted again. From both the measurements, the emanation fraction (EF) of Rn-222 was determined according to White and Rood (2001), El Afifi and Awwad (2005) and El Afifi et al. (2006):

$$\text{EF} = \frac{N}{A_0 + N} \quad (3)$$

where: A_0 and N represent the count rate of Rn-222 present in the PG samples at the first measurement (at sealing) and the second measurement (after equilibrium), respectively.

3. Results and discussion

3.1. Spectroscopic measurements

3.1.1. X-ray fluorescence

The elemental analysis by X-ray fluorescence (XRF) has been performed to determine the main elements present in the PG wastes. The data showed that the PG waste is composed of major elements (e.g., Ca, S, Si, P) and a small amount of other minor elements (e.g., Na, Al, Fe, Sr), Table 1. The major elements represent ~ 38.4 , 53.2, 5.53 and 2.05% for Ca, S, Si, and P, respectively.

3.1.2. X-ray diffraction

The X-ray diffraction (XRD) spectrum of some selected PG waste samples showed three main strong peaks at diffraction angles of

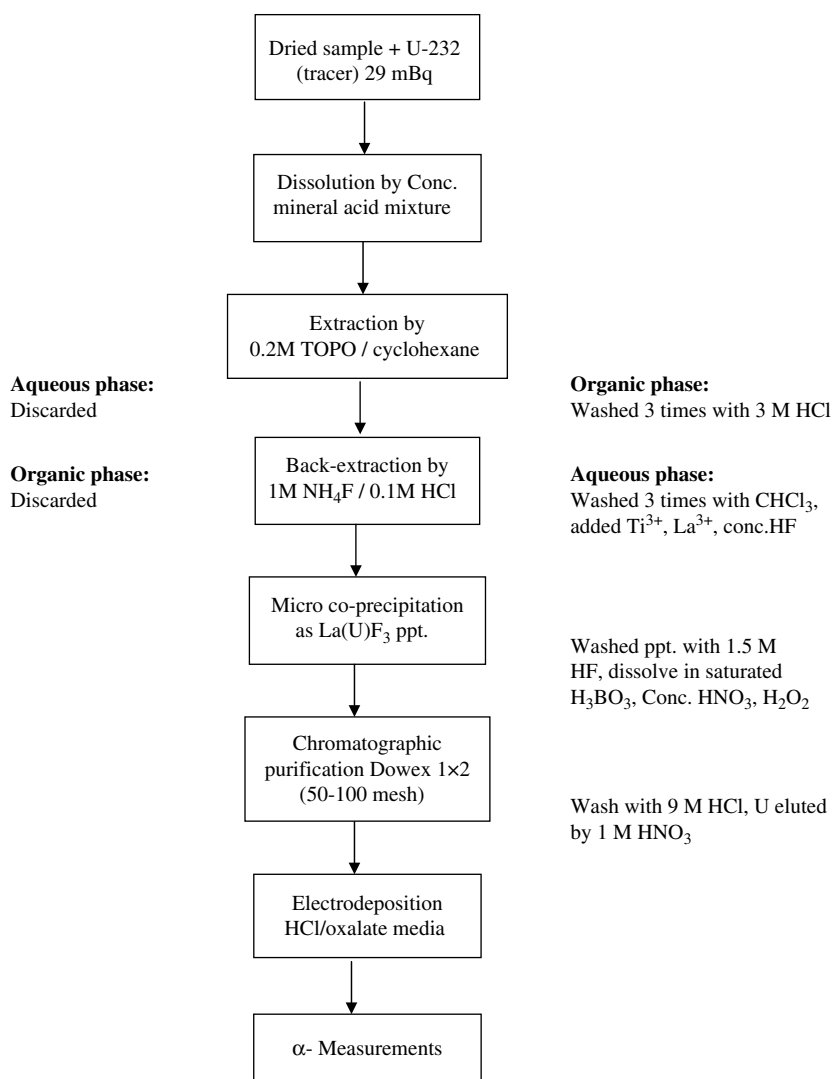


Fig. 1. Scheme of the radioanalytical procedure used for uranium separation.

14.71 ($d = 6.02 \text{ \AA}$ (angstrom)), 25.7 ($d = 3.47 \text{ \AA}$), and 29.75 ($d = 3 \text{ \AA}$). The peaks are strong and characterized by calcium sulphate (CaSO₄) as the main phase composition of the PG wastes. The other weak peaks are attributed to the presence of minor phases, such as silicate, phosphate and metallic impurities, e.g. Na, Al, Fe and Sr.

3.1.3. Infrared spectra

The IR spectra of the PG waste have been measured as potassium bromide (KBr) disc. The spectra showed many vibrational absorption bands (in cm⁻¹) characterized mainly by the inorganic sulphur compounds (S=O of SO₄²⁻) and metal-oxide bonds (M→O) as well as many types of hydroxyl groups of hydration (–OH),

silicate (Si–OH) and/or residue of phosphoric acid remaining (P–OH) in the PG wastes (Attallah, 2006).

Based on the above mentioned data of XRF, XRD and IR measurements, it is confirmed that the main phase composition of PG wastes associated with phosphoric acid produced from phosphate rock (PR) by the wet processing is calcium sulphate, CaSO₄ (92%).

Table 2

Activity concentration statistics of different radionuclides in PG and PR samples measured by γ -ray spectrometry.

Radionuclide (Bq/kg)	Samples ^a	
	PG ^b	PR ^c
	Average $\pm u^d$	Average $\pm u^d$
U-238	140 \pm 12.6	916 \pm 33.5
Ra-226	459 \pm 36.7	890 \pm 28.8
Pb-210	323 \pm 28.4	890 \pm 32.4
Th-232	8.3 \pm 0.76	34 \pm 4.7
K-40	64.3 \pm 4.1	92 \pm 10.2

^a The samples were measured three times.

^b Phosphogypsum (PG) waste samples.

^c Phosphate rock (PR) samples.

^d Combined uncertainty (u).

Table 1

The major elements found in the PG wastes using XRF analysis.

Element	Concentration (%)	Compound
Na	0.49	Na ₂ O
Al	0.23	Al ₂ O ₃
Si	5.53	SiO ₂
P	2.05	P ₂ O ₅
S	53.2	SO ₃
Ca	38.4	CaO

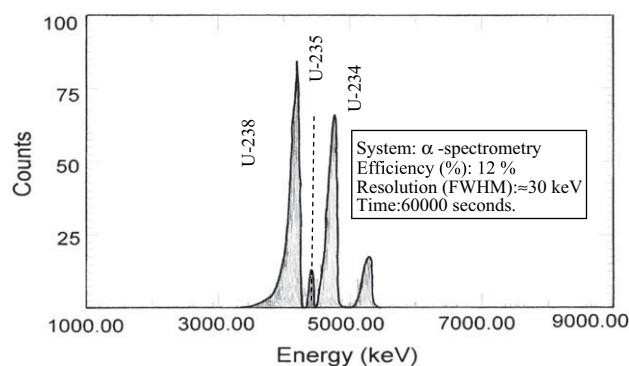


Fig. 2. A typical α -spectra of uranium isotopes measured in PG waste sample.

3.2. Radiometric measurements

3.2.1. γ -Ray measurements

Activity concentration of the different naturally occurring radionuclides of environmental interest in the phosphogypsum (PG) waste and phosphate rock (PR) samples is determined using γ -ray measurements. The results obtained are presented in Table 2. In PG waste samples, the average activity concentration of U-238, Ra-226, Pb-210, Th-232 and K-40 are 140 ± 12.6 , 459 ± 36.7 , 323 ± 28.4 , 8.3 ± 0.76 and 64.3 ± 4.1 Bq/kg, respectively. It is clear that radioactivity in the PG wastes is mainly due to radioactivities of Ra-226 and Pb-210 which represent around 93% relative to total activity. It is well known that the average worldwide activity concentration of U, Th and K-40 are 50, 50 and 500 Bq/kg, respectively (UNSCEAR, 1993). Based on this criterion, high activity concentrations of Ra-226 and/or Pb-210 (>50 Bq/kg) are found in the PG waste samples and are high comparable to those reported in other counties (UNSCEAR, 1993).

On the other hand, the average values of the activity concentration in phosphate rock (PR) samples are found to be equal to 916 ± 33.5 , 890 ± 28.8 , 890 ± 32.4 , 34 ± 4.7 and 92 ± 10.2 Bq/kg, for U-238, Ra-226, Pb-210, Th-232 and K-40, respectively. It is found that activity concentrations of U-238 and Ra-226 in the studied local samples are low in comparison with those found in literature (Saeia et al., 2005).

3.2.2. α -Measurements

Fig. 2 shows α -spectra of U source after the radiochemical procedures (Fig. 1). The spectra showed that four peaks are attributed to the natural isotopes of uranium: U-238 at 4.2 MeV (77%), U-235 at 4.4 MeV (55%), U-234 at 4.77 MeV (72%) as well as U-232 at 5.32 MeV (68.6%) of the tracer added. There is no other peak attributed to interferences associated to uranium source preparation. The average value of radiochemical recovery of the applied procedure is good and found to be equal to $\sim 70 \pm 8\%$ with resolution (FWHM) of ~ 30 KeV.

Table 3

Activity concentration statistics of uranium isotopes in PG and PR samples measured by α -ray particles spectrometry.

Radionuclide (Bq/kg)	Samples ^a	
	PG ^b	PR ^c
	Average $\pm u^d$	Average $\pm u^d$
U-238	153 ± 9.8	895 ± 83
U-235	7 ± 0.38	41 ± 3.8
U-234	152 ± 10.4	807 ± 58

^a The samples were measured three times.

^b Phosphogypsum (PG) waste samples.

^c Phosphate rock (PR) samples.

^d Combined uncertainty (u).

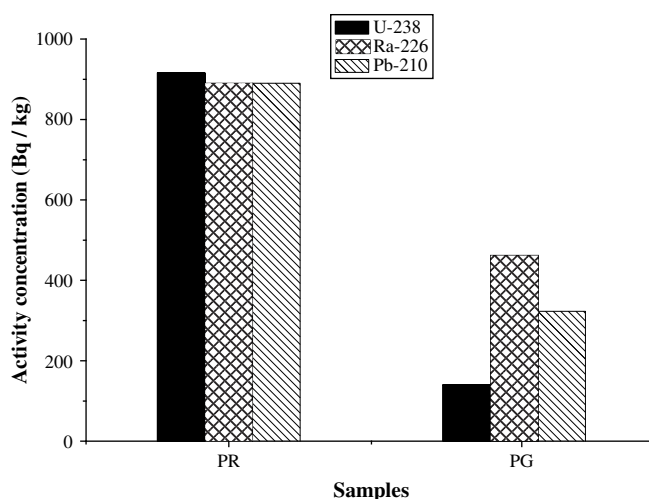


Fig. 3. Activity concentration distribution of U-238, Ra-226 and Pb-210 in PR and PG samples.

Activity concentrations of the natural uranium isotopes (U-238, U-235 and U-234) in PG waste and PR samples are determined using α -particle measurements and given in Table 3. The results showed that the average activity concentrations in some selected PG samples are found to be equal to 153 ± 9.8 , 7 ± 0.38 , 152 ± 10.4 Bq/kg for U-238, U-235 and U-234, respectively. The average value of the radiochemical recovery by the method used is good and equal to $\sim 70 \pm 8\%$. In PR samples, the average activity concentrations of U-238, U-234 and U-235 are 895 ± 83 , 41 ± 3.8 and 807 ± 58 Bq/kg, respectively.

3.2.3. Evaluation of data

Based on the previous results, it is clear that activity concentrations of U-238 found in PG wastes and PR samples determined by α - and γ -techniques are close and in agreement with each other, Tables 1 and 2. Fig. 3 shows a clear comparison related to distribution of U-series (U-238, Ra-226 and Pb-210) in PR and PG wastes associated with the wet processing of PR. To learn about the equilibrium, the parent to daughter ratio is calculated.

In PR samples, the ratios of U-238/Ra-226 and U-238/Pb-210 are found around unity (~ 1), Table 4. This is ensuring the usual equilibrium in U-series. The ratios of U-238/Ra-226 and U-238/Pb-210 are 1.06 ± 0.03 and 1.03 ± 0.04 , respectively. This value indicates that radioactive equilibrium exists between members of U-series (i.e., between U-238 and its respective decay daughters Ra-226 and Pb-210) in phosphate rock (PR) used for phosphoric acid production.

In PG waste samples, the ratios of U-238/Ra-226 and U-238/Pb-210 are found to be less than unity and equal to 0.31 ± 0.02 and 0.47 ± 0.16 , respectively. Fig. 4 shows the variations in U-238/Ra-226 and U-238/Pb-210 ratios in PG and PR samples. The variation in

Table 4

Statistics of parent/daughter ratios found in PG and PR samples based on γ -ray measurements.

Ratio	Samples ^a			
	PG ^b		PR ^c	
	Range	Average $\pm u^d$	Range	Average $\pm u^d$
U-238/Ra-226	0.25–0.35	0.31 ± 0.02	1.00–1.10	1.06 ± 0.03
U-238/Pb-210	0.22–0.62	0.47 ± 0.16	0.94–1.10	1.03 ± 0.04

^a The samples were measured three times.

^b Phosphogypsum (PG) waste samples.

^c Phosphate rock (PR) samples.

^d Combined uncertainty (u).

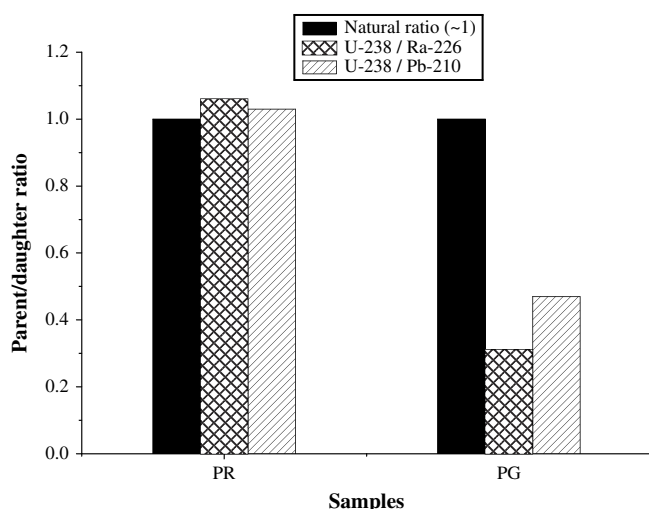


Fig. 4. Activity ratios of U-238/Ra-226 and U-238/Pb-210 in PR and PG samples.

the ratio values indicates that there is disequilibrium between U-238 and its respective long-lived progenies (Ra-226, $t_{1/2}$ 1622 and Pb-210, $t_{1/2}$ 23 years) of environmental interest. It is also observed that Ra-226 is more enhanced in the PG wastes than Pb-210. The ratio of parent/daughter is less than unity, consequently enhancement of Ra-226 and Pb-210 is attributed to attacking the PR in the wet process by concentrated H_2SO_4 . In this concern, U-series is redistributed again and fractionated. Therefore the major amounts of U migrate into phosphoric acid, while the major amounts of Ra-226 and Pb-210 remain in the PG solid wastes which present potential hazards to the surrounding environment. Therefore, the PG wastes need further studies related to treatment to reduce their environmental impacts.

The natural isotopic ratios of uranium isotopes found in PG and PR samples are calculated using α -measurements and are presented in Table 5. It is shown that the U-238/U-235 ratio is found to be equal to 21.7 ± 0.1 in both types of samples. This value is very close to the natural between U-238 and U-235 which lies within the range of 21.5–21.7 (Stadje, 1998). Also, average values of U-238/U-234 ratio are 1.00 ± 0.06 and 1.11 ± 0.05 in PG and PR samples, respectively. These values indicate that there is expected equilibrium between both isotopes. The values of U-238/U-235 and U-238/U-234 ratios in the PG waste samples are not affected during the radionuclide fractionation during the wet processing of PR.

3.3. Characteristics of the radiological indices

3.3.1. Radium equivalent index (Ra-Eq)

The radium equivalent activity was used to evaluate the actual radioactivity in the materials containing naturally occurring

Table 5

Statistics of the natural isotopic ratio of uranium isotopes found in PG and PR samples based on α -particle measurements.

Ratio	Samples ^a			
	PG ^b		PR ^c	
	Range	Average $\pm u^d$	Range	Average $\pm u^d$
U-238/U-234	0.95–1.09	1.00 ± 0.06	1.03–1.15	1.11 ± 0.05
U-238/U-235	21.60–21.80	21.70 ± 0.10	21.70–21.73	21.70 ± 0.01

^a The samples were measured three times.

^b Phosphogypsum (PG) waste samples.

^c Phosphate rock (PR) samples.

^d Combined uncertainty (u).

Table 6

Radiation hazard indices associated with PG wastes.

Statistics	Radiation hazard index		
	Ra-Eq. (Bq/kg) ^a	$D_{\gamma r}$ (nGy/h) ^b	Rn-EF ^c
Range	355–578	165–268	18–25
Average $\pm u^d$	466.7 ± 76.3	206.6 ± 35.4	22 ± 2.2
CV (%) ^e	16.3	17.1	10

^a Radium equivalent activity (Ra-Eq).

^b Absorbed gamma dose rate ($D_{\gamma r}$).

^c Radon emanation fraction (Rn-EF).

^d Combined uncertainty (u).

^e Coefficient of variance ($CV\% = SD \times 100/\text{average}$).

radionuclides, e.g. U-238 and Th-232 series, and/or K-40. Values of Ra-eq activity for the PG wastes were calculated from Eq. (1) and the results are given in Table 6. It is indicated that values of Ra-eq in the PG wastes samples are ranged between 355 and 578 Bq/kg with average value of ~ 467 Bq/kg. It is clear that the value of the Ra-eq index exceeds the maximum permissible radium equivalent activity, where, the maximum acceptable Ra-eq index in materials must be less than 370 Bq/kg as reported for safe uses in several civil purposes (Beretka and Mathew, 1985; Zaidi et al., 1991).

3.3.2. Absorbed gamma dose rate ($D_{\gamma r}$)

The total absorbed dose rate values due to the main naturally γ -emissions (i.e., Ra-226, Th-232 daughters and K-40) in the PG waste samples were calculated using Eq. (2) and are presented in Table 6. It is obvious that values of the calculated total absorbed dose rates are ranged from 165 to 268 nGy/h, with average value of ~ 207 nGy/h. It is clear that, the total absorbed dose rates are high compared to the international recommended and acceptable total absorbed dose rate (i.e. 55 nGy/h) established by UNSCEAR (2000) for the workers in the regions containing γ -radiations. The results indicated that, the total absorbed dose rates from PG waste samples under investigation are high by ~ 4 -folds relative to the acceptable and recommended safe dose level.

3.3.3. Radon emanation fraction (Rn-EF)

The radon emanation fraction is another very important radiological index, and was used to evaluate the amount of radon gas, especially Rn-222 of long half life ($t_{1/2}$ 3.84 days) comparable to the other short-lived radon gases, i.e., Rn-220 ($t_{1/2}$ 54.3 s) and/or Rn-219 ($t_{1/2}$ 3.92 s). Therefore, Rn-EF was calculated using Eq. (3) to express the amount of Rn-222 released from the PG waste materials containing enhanced activity concentrations of Ra-226 in the surrounding environment. In this concern, Rn-222 EF which was released from the surface of the PG wastes was determined through two measurements by γ -ray spectrometry. The obtained results are presented in Table 6. Amount of Rn-222 EF from the PG wastes ranged from 18 to 25% with average value of 22. This value is relatively high compared to the natural value released from soil (i.e., 20%) (Rutherford et al., 1994). Therefore, it is necessary to find suitable routes to decrease and/or redistribute the radionuclide of environmental interest (i.e., Ra-226 and/or Pb-210), in PG wastes, consequently to reduce its radiation impacts.

4. Conclusion

Solid phosphogypsum (PG) waste samples produced in a plant for fertilizer and phosphoric acid production, were characterized using spectroscopic and radiometric measurements as well as by evaluating some important radiation hazard indices. It is concluded from XRF, XRD and IR measurements that the main phase composition of the studied PG wastes is dihydrated calcium sulphate, $CaSO_4 \cdot 2H_2O$. The γ - and α -measurements showed that radium

(Ra-226) and lead (Pb-210) are the major radionuclides of environmental interest in the PG wastes with activity concentrations high compared to the recommended normal levels (50 Bq/kg). Activities of Ra-226 and Pb-210 are more than 90% relative to the minor radionuclides (i.e., U-238, Th-232 and/or K-40). Values of the activity ratios (parent/daughter) for U-238/Ra-226 and/or U-238/Pb-210 are less than unity (<1) and explain the enhancement of Ra-226 and Pb-210 in PG wastes compared to the equilibrium existing in phosphate rock (PR) samples. Values of the different radiation hazard indices (Ra-Eq, $D_{\gamma r}$ and/or Rn-EF) are high compared to the international permissible safety levels. The values found in the PG waste samples are: radium equivalent index (Ra-Eq): >370 Bq/kg, total absorbed gamma dose rate ($D_{\gamma r}$): >55 nGy/h, and radon emanation fraction (Rn-EF): $>20\%$. Based on these results, it is necessary to find suitable routes to decrease and/or redistribute radionuclide of environmental interest, such as Ra-226 and/or Pb-210 in PG wastes. These routes will be discussed in a further article.

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