Te-Norm in Phosphogypsum; Characterization and Treatment

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ABSTRACT

The present work is directed to the characterization of the phosphogypsum (PG) solid waste which accompanying the production of phosphoric acid by the wet process in Abu Zaabal company for fertilizers and chemicals production in Egypt. Samples from PG were characterized radiometrically using both γ- and α- spectrometric analysis and the different naturally occurring radionuclides present were identified. The main activity concentrations of such radionuclides were determined and the data obtained showed that this waste contains an enhanced level of some radionuclides especially Ra-226. Treatment investigations were experimented to reduce the enhanced activity level of Ra-226, which was found to exceed that permitted by the international regulations.

INTRODUCTION

The naturally occurring radioactive materials (NORM) are found everywhere. NORM represent an integral part of the planet, our bodies, the food we eat, air we breath, the places where we live and work, and within products we use. Conversely, processing of some natural resources concentrates the naturally occurring radionuclides to a degree that they may pose risks to humans and the environment. Therefore, concentrations of these radionuclides such as uranium and/or thorium series and their respective decay products in the by-products produced from several industries are 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 results from the human activities. Phosphoric acid produced from phosphate rocks by the wet process using sulphuric acid attack accounts for over 90 % of its production [1]. Accordingly, the solid wastes produced as a by-product, phosphogypsum from these processes will increase and accumulate worldwide. Phosphogypsum (PG) is composed mainly of gypsum ($CaSO_4.2H_2O$) and contains some impurities of environmental concern such as fluorides, traces elements and TE-NORM, which originate from the phosphate rocks used in this processing. Ra-226 is the major source of radioactivity in PG produced from sedimentary phosphate rocks [2]. Radioactivity present in PG can enter the environment and may pose radiation exposure concerns through several pathways [2-6]. This work is directed to the characterization of the PG waste accompanying the production of phosphoric acid by the wet process in Abu Zaabal company for fertilizers and chemicals production in Egypt. This characterization is followed by some studies on the treatment or decontamination of the produced PG waste which can be used for different purposes.

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EXPERIMENTAL

Samples Preparation

The solid PG waste samples produced as a by-product in Abu Zaabal company were collected and screened in atmospheric air for sufficient period (~ two weeks), then dried in an electric furnace at ~ 100 ^{o}C for at least 2 hours to acquire a constant weight.

Samples Fractionation

The dry PG waste was fractionated into five homogeneous fractions with different particle sizes ranged between 0.6 and 0.025 mm. This process was carried out using an automatic vibratory sieve. The effect of particle sizes on the distribution of Ra-226 and Pb-210 in the fractions was quantified by calculating the enrichment factor which is defined as the ratio of the particular radionuclides content in a certain fraction to their content in the bulk PG waste sample. Data obtained showed that most of activity levels of Ra-226 and Pb-210 are enriched in the fines of PG waste of particle sizes < 0.025 mm. The enrichment factor decreased by increasing the particle sizes till 0.6 mm. Fractions of particles sizes < 0.6 mm was found to present about 91% of the total fractions weight [7].

Samples Characterization

- ***Physical characterization***

Moisture content in PG waste was determined gravimetrically and found to be 6.8±0.6 %. Total organic matter was determined gravimetrically, based on its thermal decomposition at 380 ^{o}C [8], and found to be 9.4±0.5 %.

- ***Spectroscopic characterization***

Elemental analysis by XRF showed that PG is composed of the major elements, Ca, S, Si and P and of the minor elements, Na, Al, Fe and Sr. XRD analysis showed that the major composition of PG is calcium sulphate (~ 92 %).

- ***Radiological characterization***

The different naturally occurring radionuclides present in PG samples were identified and the concentrations of the radioactivity levels were detected and determined using a typical non-destructive nuclear technique which has been performed using γ -ray spectrometer equipped with a high pure germanium detector (HPGe) model 601, USA. The required energy and efficiency calculations for the detector were carried out using standard certified sources provided by AQCS, IAEA, Vienna. Uranium isotopes (U-238, U-235, U-234) in PG samples were determined by the destructive α -spectrometry technique after different radiochemical procedures using an EG&G Ortec α - spectrometer [7]. Validity of the data obtained was carried out using AQCS/IAEA standards.

RESULTS AND DISCUSSION

Characterization Studies

Radiological characterization

Samples from PG waste were analyzed by γ -ray spectrometer. The data obtained are given in Table I. The main activity concentrations (Bq/kg) are found to be 437±20.4, 323±15.0, 8.2±0.4 and 64.3±3.3 Bq/kg for Ra-226, Pb-210, Th-232 and K-40, respectively. The indirect determination of Ra-226 based on its daughters (Pb-214 and

Bi-214) assuming secular equilibrium conditions, was found 459±16.2 Bq/kg, Table I. Since, uranium is migrated into phosphoric acid solution during the production process using sulphuric acid solution, the trace concentration of uranium remained in PG solid waste was measured by using α -spectrometry after different radiochemical procedures. From the spectra obtained, the different radionuclides of uranium were identified and quantified. The results obtained are tabulated in Table II together with those obtained for U-238 when the same samples were measured by γ -ray spectrometry. The results indicated that the mean activity concentration in PG waste samples of U-238, U-235, U-234 were found 152.6±7.4, 7.03±0.33 and 152.3±5.6 Bq/kg, respectively, using α -spectrometry. While, the mean activity concentrations of U-238 was found ~ 140 Bq/kg using γ -ray spectrometry. The results showed that, the activity concentration of U-238 obtained by both α and γ -ray spectrometry is nearly in an agreement.

It is clear from Table I and II that, radioactivity in PG wastes is mainly due to the activities of Ra-226 and Pb-210, and represent contribution of ~ 78 % relative to the total activity present. Since the concentration of Ra-226 found in PG waste exceeds that permitted by the international regulations [9], it was found necessary to reduce the risks due to indoor radon and direct γ -radiation in PG waste to be used in different life aspects. Accordingly, some treatment studies were carried out to reduce and/or remove the enhanced activity levels of Ra-226 in the Egyptian PG wastes.

Table I. Activity Concentrations (Bq/kg, Dry Weight) of Ra-226, Th-233 Series, K-40 in Phosphogypsum (PG) Samples Measured by γ -Spectrometry

Sample code	**U-238 series**			**Th-232 Series**	**K-40**
	Ra-226 [a]	**Mean** [b]	**Pb-210**		
PG -1	356 ± 20.9	399 ± 26.5	227 ± 14.7	8.0 ± 0.8	71 ± 8.7
PG -2	368 ± 21.2	401 ± 19.5	234 ± 14.9	n.d [c]	n.d
PG -3	371 ± 21.3	388 ± 11	236 ± 15.0	20 ± 1.8	6.1 ±0.8
PG -4	347 ± 20.6	380 ± 15.5	264 ± 15.8	2.2 ± 0.4	68 ± 7.4
PG -5	404 ± 22.2	438 ± 15.5	250 ± 15.4	n.d	n.d
PG -6	422 ± 22.7	444 ± 13.5	275 ± 16.2	1.9 ± 0.3	n.d
PG -7	379 ± 21.5	423 ± 20	236 ± 15.0	n.d	3.1 ± 0.4
PG -8	517 ± 25.1	562 ± 35	630 ± 24.5	n.d	n.d
PG -9	495 ± 24.6	505 ± 2.5	627 ± 24.4	n.d	67.6 ± 7.4
PG -10	497 ± 24.6	502 ±16.5	634 ± 24.5	1.1 ± 0.2	73.7 ± 8.8
PG -11	555 ± 28.1	547 ± 2.5	150 ± 12.9	8.3 ± 0.8	150 ± 9.2
PG -12	530 ± 27.5	516 ± 16	110 ± 11.0	16.2 ± 1.5	75 ± 9.4
Range	*347-555*	*380-562*	*110-634*	*1.1-20*	*3.1-150*
Mean	*437*	*459*	*323*	*8.3*	*64.3*
SD(±) [d]	*23.4*	*16.2*	*17*	*0.9*	*6.5*

[a] From direct measurement of Ra-226 at 186.2 keV.

[b] from the average activities of its daughters (Pb-214 and Bi-214).

[c] n.d mean not detected.

[d] SD mean standard deviation.

Table II. Activity Concentrations (Bq/kg, Dry Weight) of U-isotopes in Phosphogypsum (PG) Samples measured by α -spectrometry.

Sample code	α -measurements				γ -measurements
	R % [a]	U-238	U-235	U-234	U-238
PG-1	81 ± 6.3	142.6 ± 9.7	6.6 ± 0.4	150 ± 9.7	144 ± 0.045
PG-2	62.2 ± 5.5	160.3 ± 12	7.4 ± 0.6	147 ± 11	148 ± 0.046
PG-3	65.4 ± 5.5	155 ± 11	7.1 ± 0.5	160 ± 11	127 ± 0.044
Mean	*69.53*	*152.6*	*7.03*	*152.3*	*139.7*
SD (±) [b]	*8.21*	*7.4*	*0.33*	*5.6*	*9.1*
RSD (%) [c]	*11.8*	*4.9*	*4.7*	*3.7*	*6.5*

[a] R is the recovery of uranium.
[b] SD is the standard deviation.
[c] RSD is the relative standard deviation (%).

Treatment Studies

Treatment process for PG waste was carried out based on leaching the solid waste using different reagents. The reagents used include distilled water, mineral acids solutions (HCl and HNO_3), and salts solutions of the corresponding acids. Washing process was also carried out before the recommended treatment process for optimizing the leachability process. Leachability process using distilled water showed that not more than 20 % of Ra-226 was removed under the best conditions.

- ***Treatment using mineral acids and their salts solutions***

Different concentrations from both HCl and HNO_3 solutions were tried for leaching Ra-226 from PG waste. In each case, the different parameters affecting the leaching process were studied separately. The optimum conditions obtained were as follows: solid waste of particle sizes < 0.6 mm, volume of acid solution to solid waste weight ratio is 2 L/Kg, contact time is 60 min., and temperature is 25 ^{o}C. Under such conditions the effect of different acids concentrations on the leachability percentage of Ra-226 was studied and the data obtained are illustrated in Fig. 1. It is clear from this figure that, maximum leachability of Ra-226 from PG waste occurs at 2.5 M HNO_3 solution (~ 40 %).

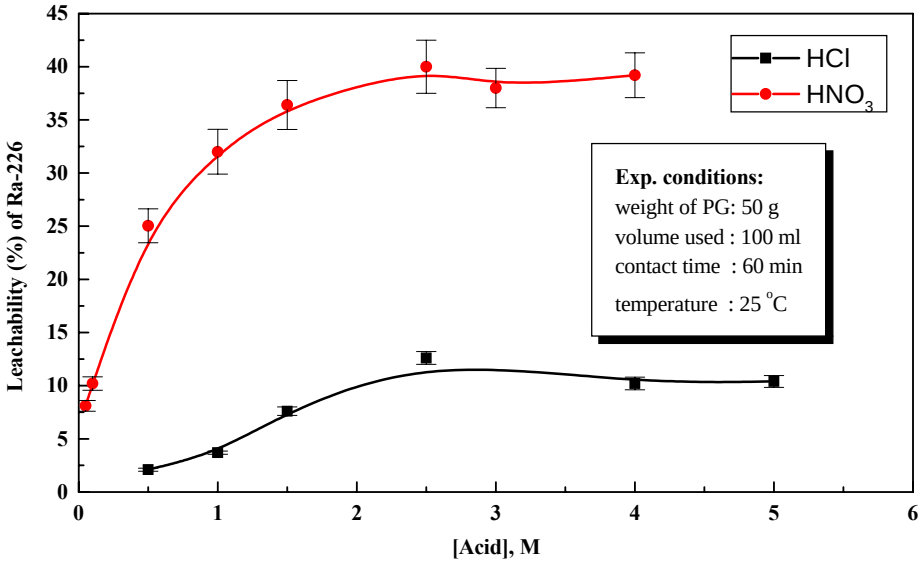

Fig.1. Effect of hydrochloric and nitric acid concentration on the leachability of Ra-226 content in PG waste.

The effect of some chlorides and nitrate salts solutions on the leachability process was also studied and the data obtained are given in Figs. 2 and 3, respectively. It is clear from both figures that, $Ca(NO_3)_2$ solution of concentration 1.5 M shows an increase in the leachability percentage (~ 48 %) compared to that obtained by 2.5 M HNO_3 solution. This result is logic since when calcium nitrate solution is used as leaching solution, calcium ions may replace Ra ions which are co-precipitated with calcium sulphate of PG sample. On the other hand, when nitric acid solution is used, the acid dissolves part of the PG sample including radium Ra-226. This was confirmed by the loss in weight observed in the treated sample Since nitric acid is a strong acid which is not recommended for leaching processes, therefore a solution based on $Ca(NO_3)_2$ was improved.

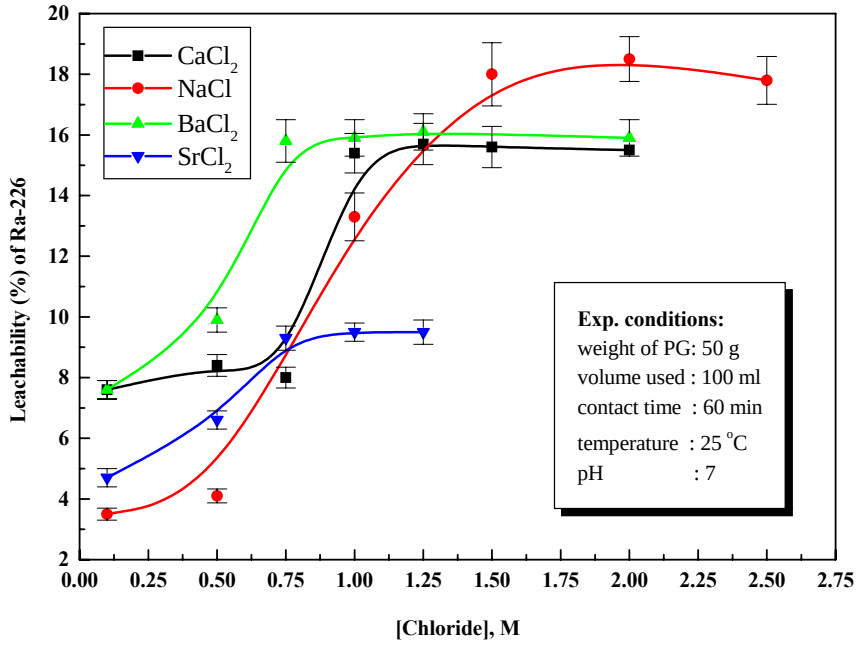

Fig. 2. Effect of chloride salts concentration on the leachability of Ra-226 content in PG waste.

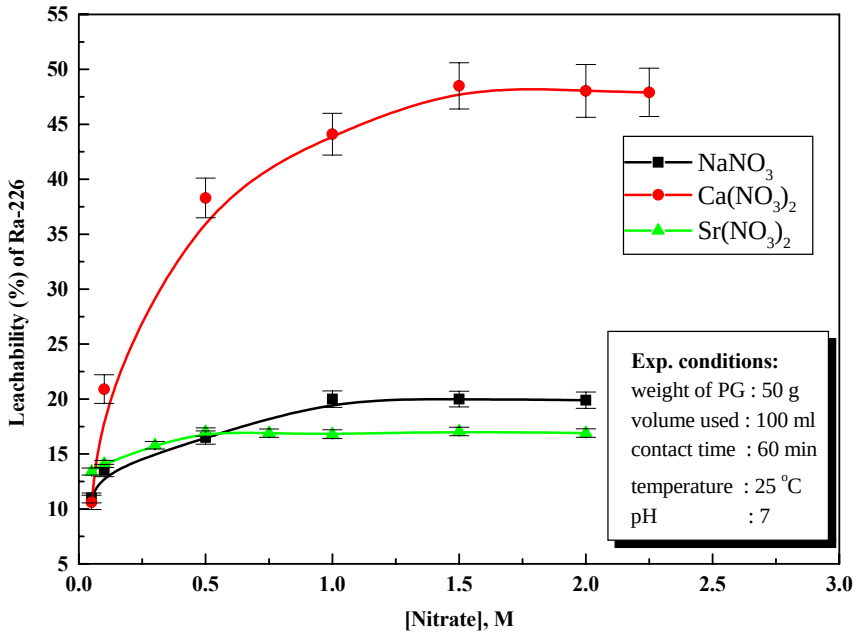

Fig. 3: Effect of nitrate salts concentration on the leachability of Ra-226 content in PG waste.

- ***Improvement of the leachability process***

In a trial to improve the leachability percentage of Ra-226 from PG waste using 1.5 M $Ca(NO_3)_2$ solution as a leaching solution, two different processes were carried out.

- ***Successive leaching processes***

In this concern, 1.5 M $Ca(NO_3)_2$ solution was used to treat the PG waste containing Ra-226 under the same experimental conditions mentioned before through successive process. The obtained results are given in Table III. it is clear that after two successive processes, about 59 % of the total Ra-226 percent in PG waste can be removed.

Table III. Successive Leaching Processes of PG Waste Containing Ra-226 Using 1.5 M $Ca(NO_3)_2$ Solution.

Leaching sequence	Leaching, %
1^{st}. step	48.5±2.1
2^{nd}. step	10.8±0.7
3^{rd}. step	----
Total	59.3±2.8

- ***Washing process***

In a trial to decrease the acidity of the PG waste before the leachability process, two different reagents were tried as washing solutions for different PG samples. These reagents were, distilled water and sodium hydroxide solution. Different concentrations and conditions were experimented. In each case, the mixture was shaken for 2 hours at 85^{o} C, cooled down at room temperature. The solid residue was separated from the mixture by centrifugation, dried and then treated with 1.5 M $Ca(NO_3)_2$ solution through two successive processes under the same optimized conditions. Data obtained showed that when the PG sample were washed with 0.05 M NaOH solution, then treated with 1.5 M $Ca(NO_3)_2$ after drying, about 89% of Ra-226 was removed . On the other hand when distilled water was used for washing the sample, only about 70% of Ra-226 was removed

CONCLUSION

It can be concluded that about 89% of Ra-226 can be removed from the phosophgypsum obtained as a solid waste from the production of phosphoric acid by the wet process. This can be achieved by washing the solid sample by 0.05 M NaOH solution followed by treating the dried sample using 1.5 M $Ca(NO_3)_2$ solution through two successive processes. Further studies will be carried out on the treatment of the contaminated aqueous solutions resulting from the PG treatment process.

REFERENCE

1. P. Becker, Phosphates and phosphoric acid: raw materials, technology and economics of the wet process. Fert. Sci.Tech. Ser., 2nd Ed., Marcel Dekker, Inc., New York, 6, 752 (1989).
2. P.M. Rutherford, M.J. Dudas and R.A. Samek, "Environmental impacts of phosphogypsum", J. Sci. Tot. Environ., 149, 1 (1994).
3. C. W. Berish. Potential environmental hazards of phosphogypsum storage in central florida, In: W. F. Chang (ed) proceedings of the 3^{rd} international symposium on phosphogypsum, Orlando, FL, Florida Institute of phosphate research, Bartow, FL, p. 1- 29 (1990).

4. J.B. Carmichael, "Worldwide production and utilization of phosphogyp-sum", In: Proc. of the 2nd Int. Symp. on phosphogypsum, Miami, FL, FIPR pub. No. 01-037-055, 1, 105 (1988).
5. M.S. Almasri and H. Suman, J. Radioanal. Nucl. Chem., 256(1), 159 (2003).
6. E.M. Hussain, "Radioactivity of phosphate ore, superphosphate, and phosphogypsum in Abu-Zaabal phosphate plant Egypt", J. Health Phys. Society, 67 (3), 280 (1994).
7. M.F. AttaAllah, M.Sc. Thesis on ‘’chemical studies on some radionuclides in industrial wastes’’, Benha university. Egypt, (2006).
8. R.P. Hesse, ‘’A Textbook of Soil Chemical Analysis’’, John Murvay, William Clowes and Sons, London, G.B. (1971).
9. J. Beretka and P. J. Mathew, J. Health Phys. Society, 48, 87 (1985).