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Treatment of Syrian Phosphogypsum using Acids and Bases

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Abstract
Phosphogypsum is a technologically enhanced naturally occurring radioactive material (TE-NORM) that contains radionuclides from ^{238}U and ^{232}Th decay series which are of most radio-toxicity. The reduction in concentration of radionuclides content from PG was based on leaching of ^{226}Ra, ^{210}Pb, U and ^{40}K using different chemicals.The factors which affect the leaching process such as leaching reagent, concentration of the proposed reagent, liquid-solid ratio, contact time, temperature and multi leaching effect were optimized. Based on the experimental results, about 79.4%, 57.9%, 65.7% and 89.8% of U, ^{226}Ra, ^{210}Pb and ^{40}K respectively, were successfully removed from the PG under optimum conditions (HNO_3, concentration (4M), liquid-solid ratio mL-gr(1-1), contact time (2h), temperature (60°C) and three leaching steps). Using this treatment of PG waste leads to obtain a decontaminated product that can be safely used in many industrial applications.
Keywords: Phosphogypsum waste, Leaching process, Radioactive materials, TENORM.

1. Introduction

Phosphogypsum (PG) is a solid waste by-product generated during the production of phosphoric acid from phosphate rocks using the "wet acid" process [1], which currently accounts for over 90% of phosphoric acid production, This process is economic however it results in the generation of a large amount of PG (for every ton of phosphoric acid produced, about 5 tons of PG are yielded) [2]. The following chemical equation (1) expresses the reaction between the phosphate rocks and sulfuric acid.

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \longrightarrow 5CaSO_4.2H_2O + 3H_3PO_4 + HF$$

Equation (1)

The annually average of PG production in India, Turkey, Korea, China, and Syria is 6, 3, 30, 22 and 0.380 million tons respectively [3, 4]. The generation of PG is up to 280 million tons per annum throughout the world [5]. However, only 15% of world PG production is recycled as building materials [6-9], agricultural fertilizers or soil stabilization amendments [10,11] and as set controller in the manufacture of Portland cement [12,13]. The remaining 85% of world PG production is disposed of without any treatment. This byproduct is usually dumped in large stockpiles exposed to weathering processes, occupying considerable land areas and causing serious environmental damage (chemical and radioactive contamination) [14-18].

Phosphogypsum is mainly consist of calcium sulphate dehydrate ($CaSO_4.2H_2O$), and it contains elevated levels of impurities, which originate from the source phosphate rock used in the phosphoric acid production. Among these impurities, radionuclides from ^{238}U and ^{232}Th decay series are of most concern due to their radio toxicity. Other elements, such as rare earth elements (REE) and Ba are also enriched in the phosphogypsum [19].

The USEPA has classified PG as a ''Technologically Enhanced Naturally Occurring Radioactive Material'' (TENORM), as it typically contains trace amounts of uranium, thorium, and daughter products from both the actinides decay chains (i.e., radium and radon) [20].

In Syria, phosphoric acid has been produced for a long time. This has led to the production of tons of phosphogypsum, which are currently placed in a large plastic lined storage pit built in 1995 near the factory in Homs (180 km N of Damascus); disposing of phosphogypsum outside this pit is currently prohibited to avoid environmental pollution. Phosphogypsum is transferred from the factory and pumped into the pit through pipes by mixing with water. The water is pumped back to the factory for re-use after filtration. However, the amount of phosphogypsum is increasing with time [4].

The treatment of phosphogypsum was discussed by many resesrchers using different leaching solutions. M. Lysandrou studied the effect of the matrix composition (main constituents) on the concentration and chemical

behavior of uranium in phosphogypsum stack solutions and leachates has been investigated [21]. A.V. Valkov tried to recover REE from PG using sulfuric acid [22]. Treatment of PG with distilled water, sulfuric acid and selective extractants (salts solutions), has been studied by M.S. Al-Masri [4]. E. M. El Afifi applied a physical (based on the particle size separation) and chemical treatment (based on leaching solutions) on PG [23].

The present study aims to purify the PG, and to decrease its radionuclides. The proposed tratment minimizes the environmental pollution of PG during storage, transportation and usage.

2. EXPERIMENTAL

2.1. Apparatus

The different naturally occurring radionuclides present in PG samples were identified and the concentrations of the radioactivity levels were detected and determined using γ-ray spectrometer equipped with Detector type: N-type model GCD - 60 230 S/N: 1479-09, manufactured by BRUKER company. The relative efficiency 60%, resolution at 1332.4 keV is 2 keV and resolution at 122 keV is 0.89 keV. The system are calibrated by using diluted CRM solution (QCY48) and QCYB 40 provided by AEA Technology, UK, and each sample counted at list for 12 hours.

shaker model LSB-030S manufactured by LabTech company with maximum shaking speed 190 rpm was used to shack the samples during the leaching processes.

2.2. Reagents and materials

All chemical materials used in this work were produced by BDH Company in analytical grade. The solutions were prepared with distilled water.

2.3. Samples Preparation

Samples of fresh PG waste were taken from an industrial facility for production of chemicals and fertilizers in Homs at February 2015. The PG waste samples were packed in plastic bags. Then the samples were dried in an electric furnace at 105°C for at least 4 h to constant weight. The PG waste samples were pulverized, homogenized and sieved into particles sizes ranged between (0.25 - 0.01mm) using an automatic vibratory screen. The concentrations of radionuclides in phosphogypsum are listed in tabel 1.

Tabel 1: Activity concentration for U, ^{226}Ra, ^{137}Cs, ^{40}K, ^{210}Pb in PG sample.

sample	Activity concentration [Bq/Kg dry PG]				
	U	^{226}Ra	^{137}Cs	^{40}K	^{210}Pb
PG	620±8	507±6	BDL	230±7	509±8

BDL: Below Detection Limit

3. Results and discussion

3.1. Treatment Studies:

In this work, treatment process for PG was carried out based on leaching the dry PG (500 gr) using different leaching reagent. The different parameters including the concentration of the proposed reagent, liquid-solid ratio, contact time, temperature and leaching steps were investigated to evaluate their affects on radionuclides leachability.

3.1.1. Effect of proposed reagent:

Many reagents, including distilled water, acids (nitric acid, sulphuric acid, hydrochloric acid, phosphoric acid, acetic acid), and alkaline (sodium hydroxide, potassium hydroxide and ammonium hydroxide), were examined to study their effects on leachability of radionuclides.

Exactly 500 gr of dried PG was divided into 4 arlenmire (250 mL) with 125 gr for each one, then 500 mL (1M concentration) of reagent was added (125 mL for each arlenmire), the solid-liquid ratio was 1-1, and the samples placed in the shaker at 50 °C for contact time 1h. The results of leachability of radionuclides (%) are tabulated in table 2. the effect of proposed reagent on the leaching process are presented in figure (1). The best leachability, achieved with HNO_3, was 29.6%, 14.2%, 18.9% and 35.3% for U, ^{226}Ra, ^{210}Pb and ^{40}K respectively.

Table 2: Effect of proposed reagent on leachability of radionuclides.

Reagent	leachability of radionuclides [%]			
	U	^{226}Ra	^{210}Pb	^{40}K
HNO_3	29.6	14.2	18.9	35.3
H_2SO_4	19.5	13.4	17.6	29.1
HCl	17.3	12.3	11.3	26.8
H_3PO_4	19.3	10.7	15.1	2.7
CH_3COOH	13.9	7.3	13.8	16.3
H_2O	7.8	3.6	5	9.2
NaOH	14.9	10.1	14.4	18
KOH	13.9	8.5	12.6	15.3
NH_4OH	8.6	6.9	10.5	12.4

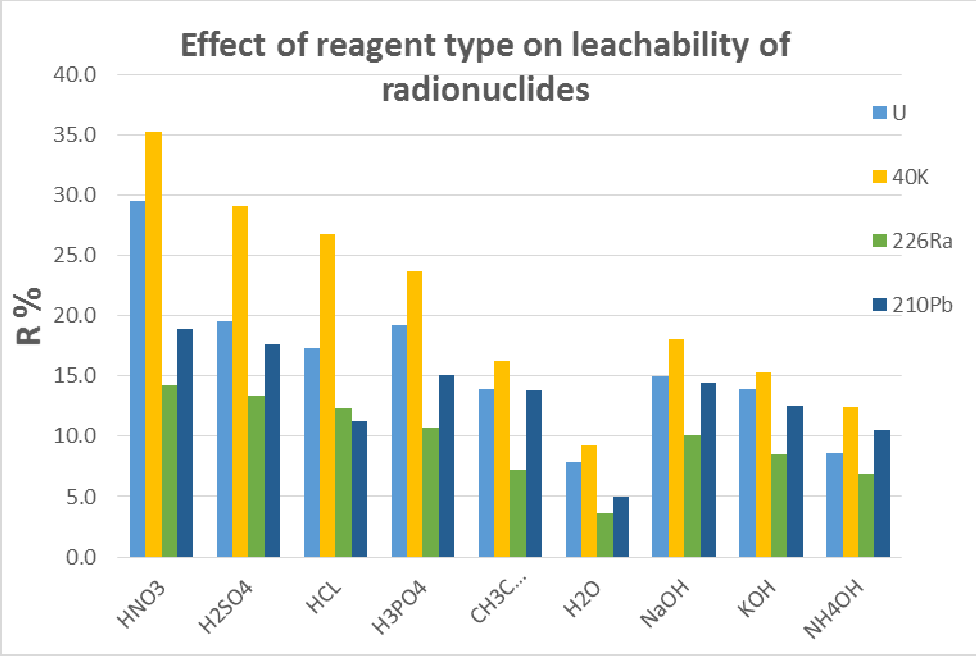

Figure (1): Effect of reagent type on leachability of radionuclides from PG.

3.1.2. Effect HNO_3 concentration:

Using nitric acid, 5 samples with different concentrations ranged between (0.5 – 10M) were prepared and treated under the same conditions. The achieved results are placed in table 3. Figure (2) illustrates the effect of HNO_3 concentration on the leachability of radionuclides (%). The best leachability, using 4M HNO_3, was 45.4%, 22.8%, 26.6% and 51.3% for U, ^{226}Ra, ^{210}Pb and ^{40} K respectively.

Table 3: Effect of HNO_3 concentration on leachability of radionuclides.

HNO_3 Concentration [M]	leachability of radionuclides [%]			
	U	^{226}Ra	^{210}Pb	^{40}K
1	29.6	14.2	48.9	35.3
2	36.2	16.7	21.3	42.4
4	45.4	22.8	26.6	51.3
8	45	19.4	23.5	49.8
10	44.8	19	22.5	51

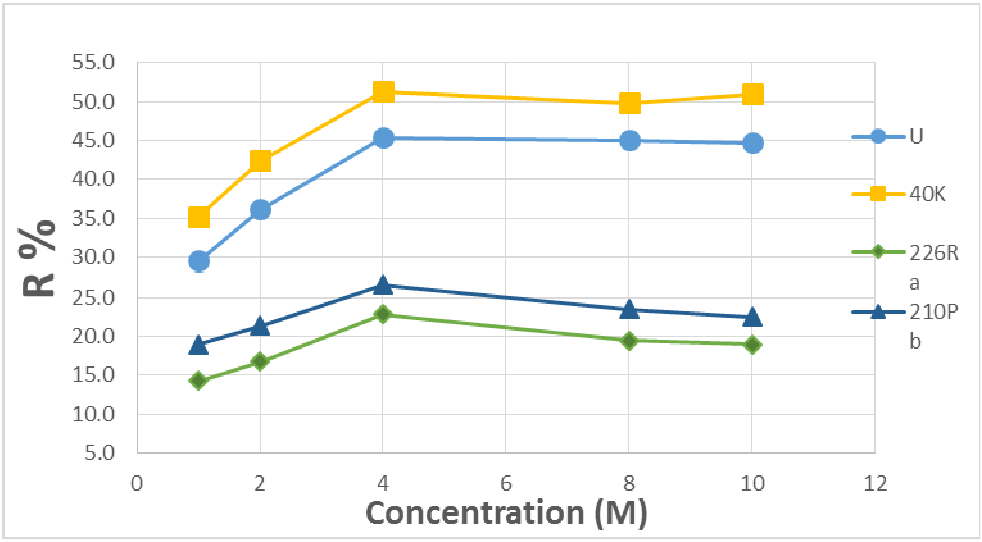

Figure (2): Effect of HNO_3 concentration on leachability of radionuclides from PG.

3.1.3. Effect of liquid -solid ratio:

Using nitric acid (4M), 3 samples with liquid-solid ratio ranged between (0.5:1 – 2:1) (L:S mL/gr) were prepared and treated under the same conditions. The obtained results are placed in table 4. Figure (3) exhibits the effect of liquid-solid ratio (mL/gr) on leachability of radionuclides (%). The best leachability, based on liquid-solid ratio 1:1 mL:gr, was 45.4%, 22.8%, 26.6% and 51.3% for U, ^{226}Ra, ^{210}Pb and ^{40} K respectively.

Table 4: Effect Liquid-solid ratio (mL/gr) on leachability of radionuclides.

Liquid-solid ratio [mL/gr]	leachability of radionuclides [%]			
	U	^{226}Ra	^{210}Pb	^{40}K
0.5	35.3	13.3	16.3	40.5
1	45.4	22.8	26.6	51.3
2	39.9	17.2	20.8	45

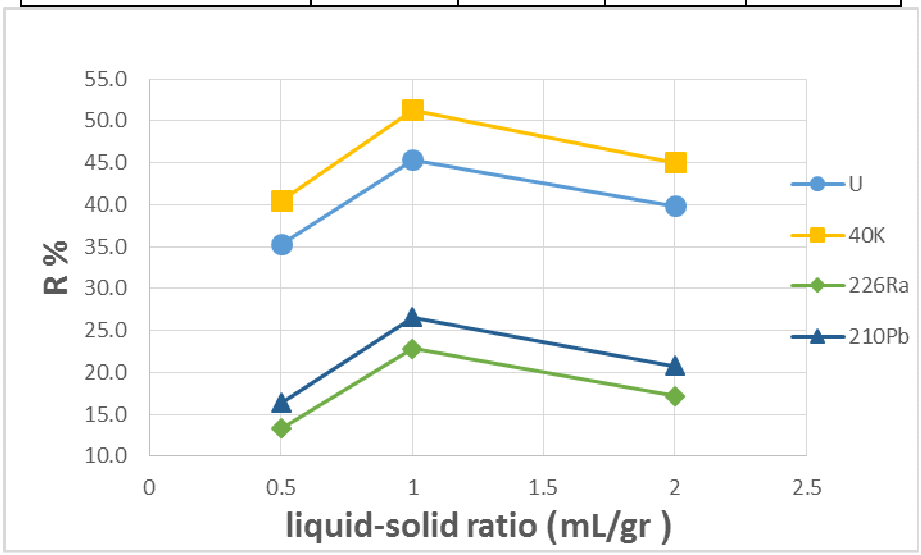

Figure (3): Effect of liquid-solid ratio on leachability of radionuclides from PG.

3.1.4. Effect of contact time:

The Effect of contact time was studied at (0.5, 1, 2, 4) h, for PG samples treated with HNO_3(4M), liquid-solid ratio 1:1 (mL:gr) at 50°C temperature. Table 5 shows the achieved results. The effects of contact time on leachability of radionuclides (%) are presented in figure (4). The best leachability was 49.7%, 27.9%, 33.3% for U, ^{226}Ra and ^{210}Pb respectively at contact time (2h), and 51.3% for ^{40} K at (4h) contact time.

Table 5: Effect of contact time on leachability of radionuclides.

Contact Time [h]	leachability of radionuclides [%]			
	U	^{226}Ra	^{210}Pb	^{40}K
0.5	39.3	13.3	21	44.4
1	45.4	22.8	27.9	51.3
2	49.7	27.9	33.3	60.1
4	48.6	27.2	32.3	63
6	49.2	27.7	33.1	59.3

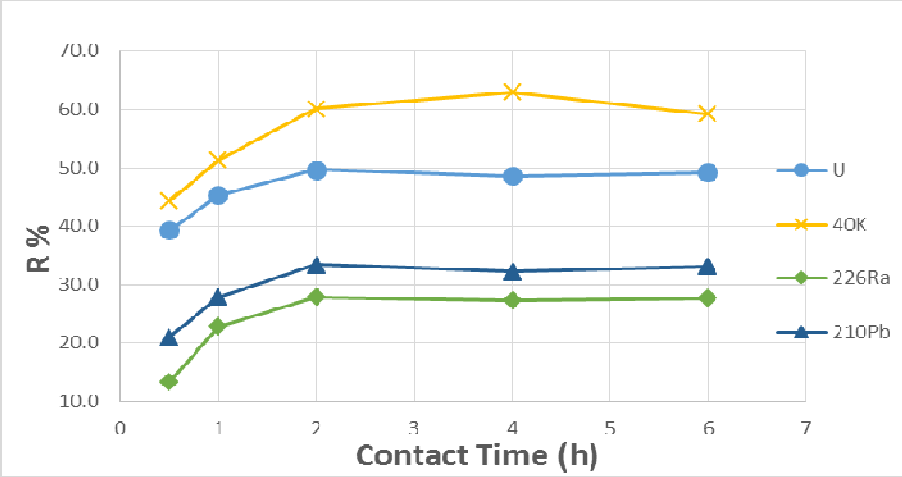

Figure (4): Effect of contact time on leachability of radionuclides from PG.

3.1.5. Effect of temperature:

The effect of temperature was studied in the range between (30-70) °C, for PG samples treated with HNO_3 (4M), liquid-solid ratio 1:1 (mL:gr) for contact time 2h. The obtained results are placed in table 6. Figure (5) demonstrates the effect of temperature on leachability of radionuclides (%). The best leachability was 50.6%, 29.7%, 34.6% and 62.2% for U, ^{226}Ra, ^{210}Pb and ^{40} K respectively at 60°C.

Table 6: Effect of temperature on leachability of radionuclides.

Temperature [°C]	leachability of radionuclides [%]			
	U	^{226}Ra	^{210}Pb	^{40}K
30	45.5	25.1	31.1	50.4
40	46.5	26.5	32.9	55.1
50	49.7	27.9	33.3	60.1
60	50.6	29.7	34.6	62.2
70	50.6	29	34.5	61.3

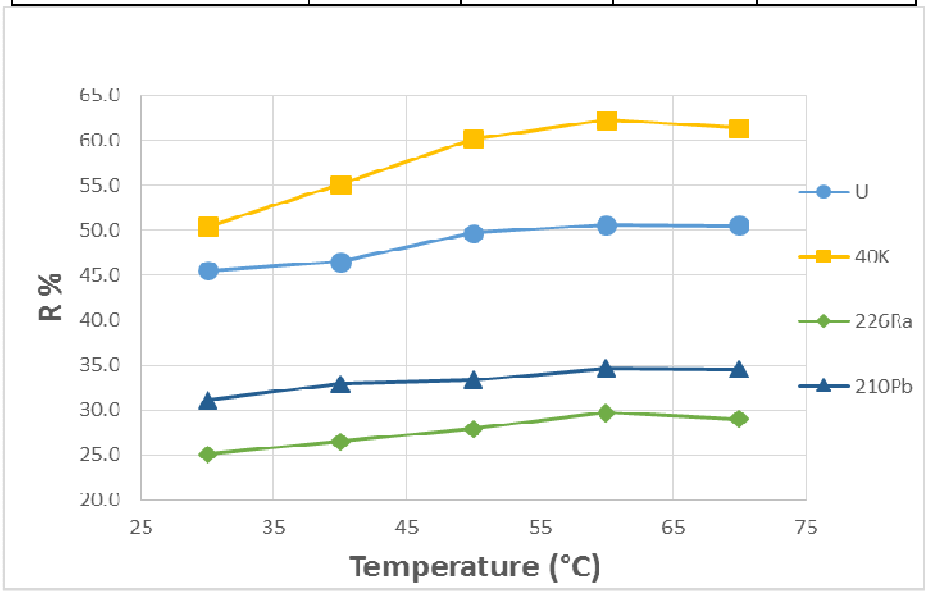

Figure (5): Effect of temperature on leachability of radionuclides from PG.

3.1.6. Effect of Successive leaching processes:

The effect of successive leaching processes was studied to reach the best leachability of radionuclides. The achieved results are placed in table 7. Figure (6) illustrates the effect of successive leaching processes on leachability of radionuclides (%). The best leachability was 79.4%, 57.9%, 65.7% and 89.8% for U, ^{226}Ra, ^{210}Pb and ^{40} K respectively at three leaching steps.

Table 7: Effect of Successive leaching processes on leachability of radionuclides.

Step process	leachability of radionuclides [%]			
	U	^{226}Ra	^{210}Pb	^{40}K
1	50.6	29.7	34.6	62.2
2	76.9	54.1	62.3	85.6
3	79.4	57.9	65.7	89.8

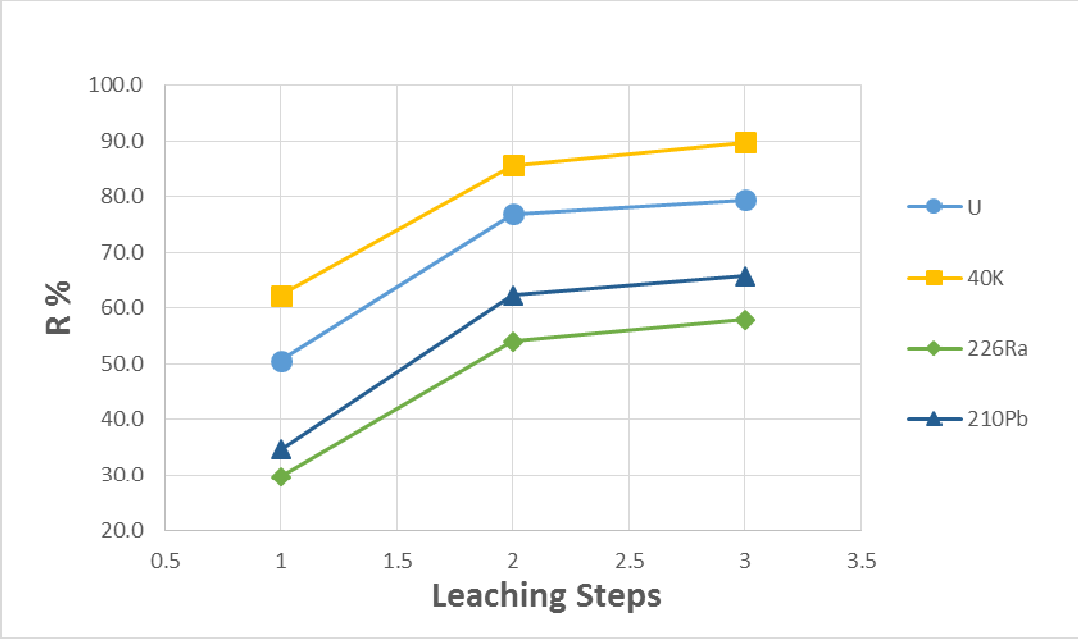

Figure (6): Effect of Successive leaching processes on leachability of radionuclides from PG.

4. Conclusions

A successful leaching procedure of phosphogypsum, a byproduct from the wet process phosphoric acid, has been developed in the present work. This was possible through leaching of radionuclides by using acids and basis. The corresponding relevant factors were studied and the conclusions can be summarized as follows:

- The best achieved leachability of U, ^{226}Ra, ^{210}Pb and ^{40} K from PG was 79.4%, 57.9%, 65.7% and 89.8% respectively.
- The optimum treatment of PG were performed using nitric acid as reagent with concentration 4M, liquid-solid ratio 1-1 (mL-gr), contact time 2h and temperature 60°C.
- The decontaminated product can be safely used in many industrial applications to prepare low cost products.

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