CHAPTER-3

RESULTS AND DISCUSSION

The results and discussion in this thesis is divided mainly into two parts, to cover the studies that carried out on the input and output materials in Abu-Zaabal Company for fertilizers and chemicals production. These materials include; i- the phosphate rocks (PR) which are used as a raw material for producing phosphoric acid, ii- the crude phosphoric acid (PA) produced, iii- the phosphogypsum (PG) produced as a solid waste and iv- the waste effluent associated with the production processes. The first part covers characterization studies on these aforementioned materials. The second part is related to some studies carried out on the treatment of the solid wastes of phosphogypsum (PG) released from this important industry, which are produced in a huge amounts and used in some life aspects. In general, both parts will be discussed in details.

3.1. Characterization Studies:

3.1.1. Radiological Characterization:

Both alpha and the non-destructive γ -ray spectrometry were used for the radiological characterization of the samples under investigation. These samples include phosphate rock (PR) samples, solid phosphogypsum (PG) samples, phosphoric acid (PA) samples as well as the waste effluent samples associated with the wet process. In γ -ray spectrometry, the samples were analyzed without any further radiochemical pre-treatment. Uranium isotopes (U-238, U-235, U-234) in PR and PG waste sample were determined also by the destructive α -spectrometry technique after different radiochemical procedures. For quality control purpose, the determinations were verified by analyzing the uranium in reagent blank samples and standard certified reference materials (AQCS/ IAEA-326 and 327) provided from IAEA, Vienna, Austria.

3.1.1.1. Phosphate rocks:

Phosphate rock (PR) is the raw material used for producing phosphorus for fertilizers, phosphoric acid (PA) and other certain chemicals in Abu Zaabal Company for phosphate fertilizers and chemical production. Some samples of the PR used were chosen randomly to cover the used PR in this Company. The activity concentrations of interested radionuclides present in these samples were measured by γ -ray spectrometry. The results obtained are given in Table (3.1). The results indicated that the average activity concentrations are 916±24.1, 866±22.8, 890±28.6, 34.1±3.5 and 92.3±8.1 Bq/kg, for U-238, Ra-226, Pb-210, Th-232 and K-40, respectively.

On the other hand, the activity concentrations of uranium isotopes in PR samples were also measured by α -spectrometry. The results showed that the mean activity concentrations of U-238, U-235 and U-234 in PR samples are 895±71, 41.2±3.24, and 807±39.9 Bq/kg, respectively, Table (3.2). It is clear that, the value of U-238 is comparable with the result obtained using measurement with γ -ray spectrometry. It is to be mentioned that the α -spectrometry measurements in this work are in agreement with those obtained for the certified references materials of AQCS/IAEA of uranium isotopes. Validation of the results obtained is given in Table (3.3). The results showed that, the activity concentration of uranium in the certified reference materials IAEA-326 and IAEA-327 are found to be 28.47±4.1, 33.1±3.5 Bq/kg for U-238 respectively, and 29.06±4.15, 32.4±3.5 Bq/kg for U-234 respectively. These values are in agreement for the certified values of U-238 and U-234, Table (3.3) [94].

From the data obtained, it can be concluded that the total radioactivity in the PR is mainly due to activities of uranium chain (U-238, Ra-226 and Pb-210). The activities of U-238, Ra-226 and Pb-210 in the PR are about 95.5 %, while Th-232 and K-40 represent only about 4.5 %. To learn about the equilibrium, the parent/daughter ratio was calculated and given in Table (3.1). The U-238/Ra-226 and U-238/Pb-210 ratios in the PR are ranged from 1 to 1.21 (av. 1.06) and 0.93 to 1.17 (av. 1.04), respectively. This showed that, radioactive equilibrium is existed between U-238 and its daughters (i.e., Ra-226 and Pb-210) in the Egyptian PR.

Some of the previously reported results for the activity concentration of the natural radionuclides in the PR of different origins are presented in Table (3.4). For comparison, the radioactivity due to U-238, and Ra-226 in the Egyptian PR used in Abu Zaabal Company are found 916 and 866 Bq/kg, respectively. This value is lower than those reported in other countries e.g., Morocco, Togo, USA (Florida), Jordan, Israel, Tanzania, Sudan (Uro), and Greece and is higher than those found in Brazil and Senegal (for U-238), Table (3.4) [104-110].

Table (3.1): Activity concentrations (Bq/kg, dry weight) of U-238, Th-232 series and K-40, and activity ratio of U-238/Ra -226 and U-238/Pb-210 in phosphate rock (PR) samples measured by γ -spectrometry.

Sample code	U-238 series				Th-232 series	K-40	U-238/ Ra-226	U-238/ Pb-210
	U-238	Ra-226[a]	Mean[b]	Pb-210				
PR-1	992 ± 25	910 ± 33	913 ± 16	923 ± 29	25 ± 3.6	96 ± 8.9	1.09	1.08
PR-2	902 ± 24	863 ± 32	891 ± 11	973 ± 30	27 ± 3.3	n.d	1.05	0.93
PR-3	816 ± 23	829 ± 31	825 ± 11	836 ± 28	30 ± 3.5	102 ± 10	1.0	1.0
PR-4	920 ± 24	888 ± 33	894 ± 4	848 ± 28	24 ± 3.2	51 ± 8.5	1.04	1.09
PR-5	903 ± 24	888 ± 33	888 ± 12	874 ± 28	34 ± 3.7	113 ± 8.4	1.02	1.03
PR-6	843 ± 23	868 ± 32	906 ± 34	879 ± 29	28 ± 3.7	104 ± 7.7	1.0	1.0
PR-7	982 ± 25	867 ± 32	869 ± 5	912 ± 29	50 ± 3.6	90 ± 6.3	1.13	1.08
PR-8	842 ± 23	856 ± 32	885 ± 12	875 ± 28	25 ± 3.3	n.d	1.0	1.0
PR-9	1018 ± 25	839 ± 32	917 ± 45	869 ± 28	49 ± 3.3	66 ± 6.4	1.21	1.17
PR-10	940 ± 25	856 ± 32	900 ± 35	911 ± 29	49 ± 4.0	116 ± 8.6	1.1	1.03
Range	816-1018	829-910	825-917	836-973	24.2- 49.7	51-116	1.0-1.21	0.93-1.17
Mean	916	866	889	890	34.1	92.3	1.064	1.041
SD (±)	24.1	22.8	18.5	28.6	3.5	8.1	0.065	0.063

a: from direct measurement of Ra-226 at 186.2 keV, b: from the average activities of its daughters (Pb-214 and Bi-214), n.d: not detected, and SD: standard deviation, Table (3.2): Activity concentration of uranium isotopes in PR samples determined by α -spectrometry.

Sample	Activity Bq/kg		
	U-238	U-235	U-234
PR-1	823±80	37.9±3.7	800±79
PR-2	871±85	40.1±3.9	762±80
PR-3	991±97	45.6±4.5	859±90
Mean	895	41.2	807
SD (±)	71	3.24	39.9
RSD (%)	7.9	7.8	4.9

Table (3.3): Validation of α -spectrometry for determination of uranium isotopes using AQCS/IAEA samples

Sample	Certified activity Bq/kg			Found activity Bq/kg		
	U-238	U-235	U-234	U-238	U-235	U-234
IAEA-236	29.4	NR*	29.3	28.47±4.1	1.3±0.2	29.06±4.15
IAEA-327	32.8	NR*	31.9	33.1±3.5	1.5±0.16	32.4±3.5

* NR: not reported in the certificate reference sample.

Table (3.4): The reported activity concentrations (Bq/kg) in PR from different countries.

Country	U-238	Ra-226	References
Morocco	1700	1600	[104]
Togo	1300	1100	[104]
USA (Florida)	1500	1600	[104]
Jordon	--*	1044	[105]
Israel	--*	1825	[105]
Tanzania	4641	5022	[106]
Senegal	705	1025	[107]
Sudan (Uro)	4131	4021	[108]
Brazil	638	723	[109]
Greece	984	1050	[110]
Egypt	916	866	The present work

* Not reported

3.1.1.2. Phosphoric acid:

Most uranium in PR is partitionated into the phosphoric acid (PA) during the acidulation process. However, the partitioning is affected by redox conditions and the presence of other ions [20]. Since, uranium has radiological and chemical hazardous, it is important to be determined in the PA produced from the wet process.

For this purpose, different samples from the crude phosphoric acid (PA) produced by the wet process associated with the phosphate fertilizers and chemical production in Abu Zaabal Company were taken for radiometric analysis by γ -ray spectrometer. The obtained results of these samples are given in Table (3.5).

The results showed that the mean activity concentrations (Bq/kg) of the different radionuclides were found 1590±30.2, 15.9±1.2, 21.5±1.3, 18.8±1.5 and 42.5±4.2 Bq/kg for U-238, Ra-226, Pb-210, Th-232 and K-40, respectively. It is clear that, ~ 94.2 % of the total radioactivity in the PA is mainly due to contribution from the activity of U-238. While the contribution of the other radionuclides (Ra-226, Pb-210, Th-232 and K-40) represents ~ 5.8 %.

The activity concentrations of U-238 and Ra-226 in PA during processing of PR in different countries are reported and given in Table (3.6) [110]. For comparison, the obtained results indicated that the radioactivity in PA produced in Egypt due to U-238 is lower than that in other countries e.g., Morocco, Israel and higher than that found in Greece [110]. From the results obtained, the calculated enriched factors U-238/Ra-226 and U-238/Pb-210 are found 131.5 and 103.43, respectively, Table (3.5). This value is higher than those found in other countries [110]. The higher enriched factor of U/Ra in PA means that U-238 migrated into PA during the processing of PR, while Ra-226 is transferred into the solid phase of PG wastes. Therefore, PG is a by-product waste, which considered as a TE-NORM during the production of PA produced by the wet process.

Table (3.5): Activity concentrations (Bq/kg) of U-238 and Th-232 series, K-40, and activity ratio of U-238/Ra-226 and U-238/Pb-210 in phosphoric acid (PA) samples measured by γ -spectrometry.

Sample code	U-238 series			Th-232 series	K-40	U-238/ Ra-226	U-238/ Pb-210
	U-238	Ra-226	Pb-210				
PA-1	1588 ± 30	7.0 ± 1.0	n.d	13.0 ± 1.1	47.7 ± 4.9	227	n.d
PA-2	1589 ± 30	13.9 ± 1.7	12.9 ± 1.0	21.4 ± 1.8	14.9 ± 1.70	114	123
PA-3	1590 ± 30	30.0 ± 1.6	40.6 ± 1.8	23.4 ± 2.1	n.d	53	39.2
PA-4	1512 ± 30	8.4 ± 0.8	8.30 ± 0.9	19.3 ± 1.4	47.7 ± 4.9	180	182
PA-5	1669 ± 31	20.0 ± 1.1	24.0 ± 1.5	16.8 ± 1.2	59.7 ± 5.3	83.5	69.5
Range	1512-1669	7-30	8.3-40.6	13 – 23.4	14.9 – 59.7	53 – 227	39.2 – 182
Mean	1590	15.9	21.5	18.8	42.5	131.5	103.43
SD (±)	30.2	1.2	1.3	1.5	4.2	63.6	54.3

n.d: not detected, SD: standard deviation.

Table (3.6): The reported activity concentrations (Bq/kg) of U-238 and Ra-226 in PA from different countries.

Country	Activity concentration (Bq/kg)		References
	U-238	Ra-226	
Greece	1310	677	[114]
Morocco	1780	1166	[114]
Israel	2260	1290	[114]
Egypt	1590	15.9	The present work

3.1.1.3. Phosphogypsum (PG):

Samples from the solid PG wastes produced as a by-product in Abu Zaabal Company for fertilizers and chemical materials production were analyzed by γ -ray spectrometry. The obtained results are given in Table (3.7). The results showed that, the mean activity concentration (Bq/kg) found in the PG wastes are 437±23.4, 323±17, 8.3±0.9 and 64.3±6.5 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, Table (3.7). Both measurements of Ra-226 are closed together. Fig. (3.1) shows a γ -ray spectra having regions of interest related to the naturally occurring radionuclides in the PG samples.

Since, uranium is migrated into PA, the trace concentration of uranium remained in PG waste was measured by using the α -spectrometry after different radiochemical procedures. Fig. (3.2) shows a typical α -spectra of uranium isotopes in PG samples measured by EG&G ORTEC α -spectrometry. From these spectra, the different radionuclides were identified and quantified. The obtained results are tabulated in Table (3.8). 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. While, the mean activity concentrations of U-238 was found ~ 140 Bq/kg, when the same samples were measured by 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 that, radioactivity in PG wastes is mainly due to the radioactivities of Ra-226 and Pb-210, and represent contribution of ~ 78 % relative to the total activity present. While the contribution of U-238, Th-232 and K-40 represent ~ 22 %.

For comparison, activity concentrations of Ra-226 reported in PG wastes in different origins are given in Table (3.9). The activity concentration of Ra-226 of PG in this work is 437 Bq/kg. This value is higher than those reported in other countries e.g., Greece [110], Syria [80], and lower than those found in USA [42], Candia [20], Australia [23], Hungary [111], Senegal, Morocco [107], and Brazil [109].

In this study, the activity ratio of uranium (U-238) and its long-lived daughters (i.e., Ra-226, Pb-210) was calculated and the results are listed in Table (3.10). The results showed that the activity ratios of U-238/Ra-226 and

Table (3.7): 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	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(±)	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),
n.d: not detected,
SD: standard deviation.

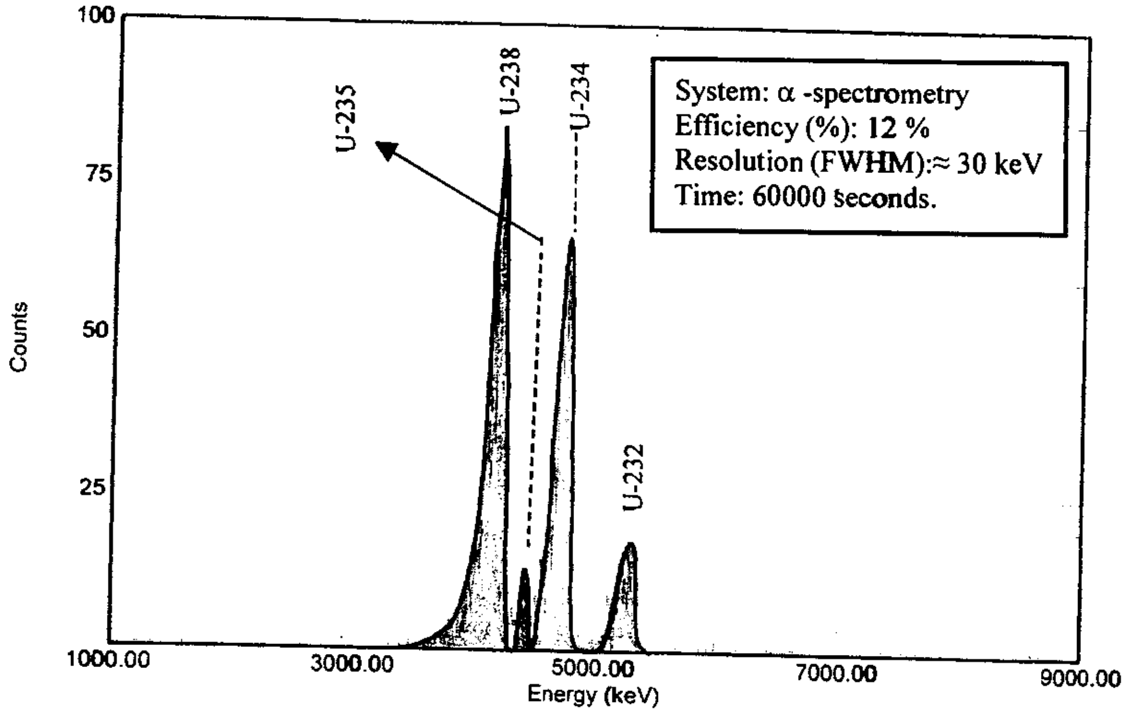

Fig. (3.2): A typical α -spectra of uranium isotopes measured in PG waste sample.

Table (3.8): Activity concentrations (Bq/kg, dry weight) of U-isotopes in phosphogypsum (PG) samples measured by α -spectrometry.

Sample code	α -measurements				γ -measurements
	R %	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 (±)	8.21	7.4	0.33	5.6	9.1
RSD (%)	11.8	4.9	4.7	3.7	6.5

R: is the recovery of uranium, SD: standard deviation and RSD: is the relative standard deviation (%).

Table (3.9): Activity concentrations (Bq/kg) of Ra-226 in PG wastes reported in different countries.

Country	Ra-226	References
Candia: (Alberta)	890	[20]
Australia	500	[23]
USA (Florida)	1140	[42]
Hungary	1093	[111]
Senegal	518	[107]
Morocco	618	[107]
Greece	380	[110]
Brazil	700	[109]
Syria	310	[80]
Egypt	437	The present work

Table (3.10): Activity ratio of U-238/Ra-226 and U-238/Pb-210 in PG wastes

Sample code	U-238/Ra-226	U-238/Pb-210
PG-1	0.39	0.62
PG-2	0.38	0.60
PG-3	0.38	0.59
PG-4	0.40	0.53
PG-5	0.35	0.56
PG-6	0.33	0.51
PG-7	0.37	0.59
PG-8	0.27	0.22
PG-9	0.28	0.22
PG-10	0.28	0.22
PG-11	0.25	0.93
PG-12	0.26	1.27
Range	0.25-0.40	0.22-1.27
Mean	0.33	0.57
SD (±)	0.054	0.29

U-238/Pb-210 in the PG wastes are ranged from 0.25 to 0.4 (average 0.33) and 0.22 to 1.27 (average 0.57), respectively, Table (3.10). It is clear that these radionuclides U-238, Ra-226 and Pb-210 are far away from the radioactive equilibrium. The lower values of U-238/Ra-226 and U-238/Pb-210 than unity indicate the enhancement of Ra-226 and Pb-210 in PG which considered as TE-NORM wastes, during the processing of PR to produce PA.

Based on the previous results of the PR, PA and PG, it can be concluded that, the major radioactivity is due to the presence of U-238, Ra-226 and Pb-210 in PR, U-238 in PA, and Ra-226 and Pb-210 in PG wastes. The minor radioactivities were found for Th-232, K-40 in PR, Ra-226, Pb-210, Th-232, K-40 in PA and U-238, Th-232, K-40 in PG wastes. Fig. (3.3) shows the actual distribution of activity concentration of the interested radionuclides in PR, PA, and PG waste.

The international regulations, the US EPA stated that PG would be permitted for use in agriculture if the average concentration of Ra-226 in the PG does not exceed 370 Bq/kg [20]. This limit was set to reduce the risks due to indoor radon and direct γ -radiation in residences constructed on land treated with PG waste. The average activity concentration of Ra-226 in the Egyptian PG wastes is higher than the limit value to use PG wastes in the different life aspects according to regulations of US EPA. This value is also higher than a normal activity (i.e., 50 Bq/kg) of Ra-226 in soil as stated by UNSCEAR, [10,40,112,113]. For this reason, activity of Ra-226 in PG wastes should be reduced. In the present work some studies were carried out to reduce and/or remove the enhanced activity levels of Ra-226 in PG wastes.

3.1.1.4. Waste effluents:

The main physicochemical characteristic of the waste effluent samples associated with the production of phosphate fertilizers in Abu Zaabal Company is determined and presented in Table (3.11). The data obtained showed that, the pH of waste effluent sample is acidic and ranged between 2.8 and 2.91 with the mean value 2.86±0.02. These values are less than the pH limit values (6.5-8.5) recommended by US EPA and WHO [20,114]. This acidity is due to the residue of H_2SO_4 and/or H_3PO_4 (PA) during the wet process.

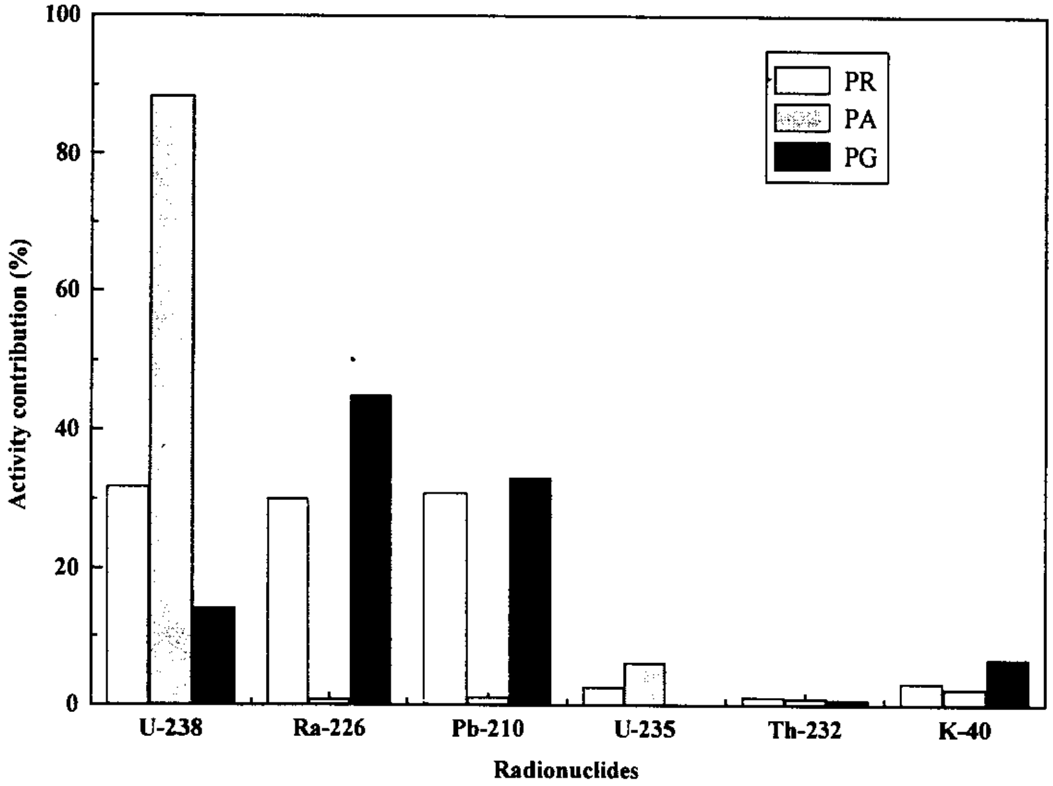

Fig. (3.3): Activity contribution (%) of the interested radionuclides in PR, PA and PG.

Table (3.11): Some physical and chemical characteristics of the waste effluent produced from Abu Zaabal Company for phosphate fertilizers and chemicals production.

Properties	Value	Recommended value*	References
pH	2.86±0.02	6.5-8.5	[20,114]
TDS (mg/L)[a]	1310±65	500 mg/L	[20,114]
Ca^{2+} (mg/L)	1202±100	250 mg/L	[115]
Mg^{2+} (mg/L)	952±150	50 mg/L	[115]
EC (μS. cm^{-1})[b]	3297±200	1500	[115]
Cl^- (mg/L)	360±85[c] 379.6±18[d]	250 mg/L	[20,114]
SO_4^{-2} (mg/L)	2580±99	250 mg/L	[20,114]
F^- (mg/L)	412.9±20	4.0 mg/L	[20,114]
NO_3^- (mg/L)	74.7±5	10.0 mg/L	[20,114]
Uranium (mg/L)	24.1±2	0.8 mg/L	[116]

a: TDS (total dissolved solids) was determined gravimetrically,
b: EC (electric conductivity) was determined at 16 °C,
c: the result obtained by gravimetric analysis,
d: the result obtained by IC, and
*: the reported recommended values established by US EPA, United Kingdom (UK) and/or WHO.

The total dissolved solid (TDS) in waste effluent samples was determined gravimetrically and gives a mean value of 1310±65 mg/L. This value is higher than the acceptable limit value of 500 mg/L [20,114]. The hardness due to presence of Ca^{2+} and Mg^{2+} in waste effluent samples was determined using complexmetric titration using EDTA solution. The mean concentration of Ca^{2+} and Mg^{2+} were found 1202±100 and 952±150 mg/L, respectively (Table 3.11). These levels are high comparable to the permissible levels 250, 50 mg/L for Ca^{2+} and Mg^{2+}, respectively, which are established by the United Kingdom [115]. The average value of electric conductivity (EC) of the waste effluent samples was 3297±200 µS/cm. This value is high compared to the normal level of EC, which does not exceed 1500 µS/cm [115].

The chloride and sulphate concentrations in waste effluent were found 360±85 mg/L, 2580±99 mg/L, respectively. Concentrations of fluoride, nitrate, and chloride anions were found ~ 413, 75, and 380 mg/L, respecttively. Values of these anions are higher than those acceptable levels [20,114]. The total uranium concentration in the waste effluent was measured spectrophotometrically using Arsenazo-III as previously mentioned in section (2.6.5). The concentration obtained was found to be ~ 24±2 mg/L which is higher than the recommended limit (0.8 mg/L) [116].

Activity concentrations (Bq/L) of natural radionuclides in waste effluent are measured by γ -ray spectrometry, the results are given in Table (3.12). The obtained result indicated that the activity concentration of Ra-226, Pb-214, and Pb-210 are equal to 19.3±1.5, 14.9±1.2, and 17.2±1.3 Bq/L, respectively. The activity concentration of Ra-226 in waste effluent is higher than the reported value (1 Bq/L) by the Canadian maximum acceptance limit [20].

Based on the obtained results, the waste effluent associated with the wet-process has high levels of different contaminants. Therefore, the waste effluent in its original state cannot be used for the human and/or agriculture purposes and needs further treatment.

Table (3.12): The activity concentration (Bq/L) of natural radionuclides in waste effluent samples.

Radionuclide of interest	Activity concentration Bq/L (mean ± SD)
Ra-226	19.3±1.5
Pb-214	14.9±1.2
Pb-210	17.2±1.3

Based on the previous results obtained from the radiological characterization studies on the different input and output materials in Abu Zaabal Company for fertilizers and chemicals production, the following can be concluded:

i- The major radioactivity is due to the presence of U-238, Ra-226 and Pb-210 in PR, U-238 in PA, and Ra-226 and Pb-210 in PG wastes.

ii- The waste effluent associated with the wet-process has high levels of different contaminants. Therefore, the waste effluent in its original state cannot be used for the human and/or agriculture purposes and needs further treatment.

iii- The average activity concentration of Ra-226 in PG waste (437 Bq/kg) is higher than the limit of the permissible safe value reported for the use of PG in the different life aspects [20].

Therefore, studies on the general characterization and treatment of PG wastes will be carried out and discussed in details.

3.1.2. General Characterization of PG:

3.1.2.1. Physical characterization:

3.1.2.1.1. Moisture content:

The moisture content in PG waste means the water molecules, which are bounded with the particles by Van der Wall's forces [67]. Generally, the moisture content has been determined gravimetrically in PG wastes and was found to be 6.8±0.7 %.

3.1.2.1.2. Total organic matter (TOM):

The organic matter content in PG wastes has been determined using gravimetric method based on thermal decomposition of the organic matters at 380 °C as described by Ball and Hesse [67,82]. The total organic matter present in PG was found to be 9.4±0.5 %.

3.1.2.1.3. Fractionation process:

In this concern, the PG wastes was fractionated into five homogeneous fractions with different particle sizes ranged between 0.6 and 0.025 mm, to show the effect of particle sizes on the distribution of Ra-226 and Pb-210 in the samples. This effect is quantified by calculating an enrichment factor (EF) which is defined as the ratio of particular radionuclide content in a certain fraction over the content of that species in the bulk PG waste.

The fractionation process is carried out using two different techniques, these are: a) dry sieving fractionation, and b) wet sieving fractionation. The obtained results of both techniques are given in Table (3.13), which shows the weight percent of each fraction relative to the total amount of the bulk PG wastes.

The total recovery percent of the homogenized and non-homogenized parts of PG was 99.8 and 95.9 %, in case of the dry and wet sieving, respectively. The rest parts were loosed as a dust and/or solubilization amount of PG waste at the sieving processes. In the dry sieving, the large fractions of particle sizes 0.053-0.15 mm represented ~ 49 %, while the lower fractions of particle sizes < 0.025 mm represented 0.3 %. In case of wet sieving, the large fractions of particle sizes 0.15-0.25 mm represented 33.4 %, and the lower fraction, 0.025-0.053 mm, represented 2 %. On the other hand, the nonhomogenized fractions represent 8.5 and 3.4 % for dry and wet fractionation, respectively.

Table (3.13): Data of the dry and wet sieving fractionation of PG wastes.

Fraction (mm)[a]	Wt. (%) ± SD	
	Dry sieving	Wet sieving
F1 (<0.025),	0.3±0.02	7.4±0.2
F2 (0.025-0.053),	7.8±0.6	2.0±0.2
F3 (0.053-0.15),	48.9±1.2	21.1±0.7
F4 (0.15-0.25),	26.3±1.0	33.4±1.5
F5 (0.25-0.6).	8.0±0.4	28.6±0.2
Nonhomogenized[b]	8.5±0.4	3.4±0.4
Recovery	99.8±3.9	95.9±12.5

a: homogenized fractions (F1-F5) with recovery of 91.3 % and 92.5 % for dry and wet sieving respectively, and

b: nonhomogenized PG over the vibratory siever is 8.5% and 3.4 % for dry and wet sieving respectively.

The distribution of the interested radionuclides in the different fractions was evaluated by calculating the enrichment factors as described before. The results are presented in Figs. (3.4) and (3.5). The results indicated that, the enrichment factors in fines of PG waste (< 0.025 mm) are reached to 1.66 and 2.46-folds in case of the dry sieving for Ra-226 and Pb-210, respectively. The enrichment factors are increased to 3.1 and 3.9-folds at the wet sieving, Figs. (3.4) and (3.5). These results indicated that, most activity levels of Ra-226 and Pb-210 are enriched in the fines of PG wastes of the particle sizes less than 0.025 mm, comparable to that found in the bulk of PG waste. The enrichment factors are decreased by the dry and wet sieving in the PG waste greater than 0.025 mm. It is clear that, the dry and wet fractionation can be considered as a physical separation of the most interested radionuclides (Ra-226 and Pb-210) in the PG waste.

3.1.2.2. Spectroscopic characterization:

3.1.2.2.1. X –ray diffraction:

Spectrum of the X –ray diffraction of the PG waste sample is presented in Fig. (3.6). The spectrum showed a main three strong peaks at diffraction angles of 14.71 (d = 6.02 Å (angstrom)), 25.7 (d = 3.47 Å), and 29.75 (d = 3 Å). These strong peaks are characterized to calcium sulphate as the 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.

3.1.2.2.2. X –ray fluorescence:

The elemental analysis by X –ray fluorescence (XRF) has been performed to determine the main elements present in the PG waste sample. The obtained data is given in Table (3.14). The data showed that the PG waste is composed of major elements, (Ca, S, Si, P) and a small amount of other minor elements (Na, Al, Fe, Sr). The major elements represent ~ 38.4, 53.2, 5.53 and 2.05 % for Ca, S, Si, and P, respectively. Data of XRF and XRD confirmed that the main phase composition of PG wastes associated with the wet processing of PR is calcium sulphate (~ 92 %).

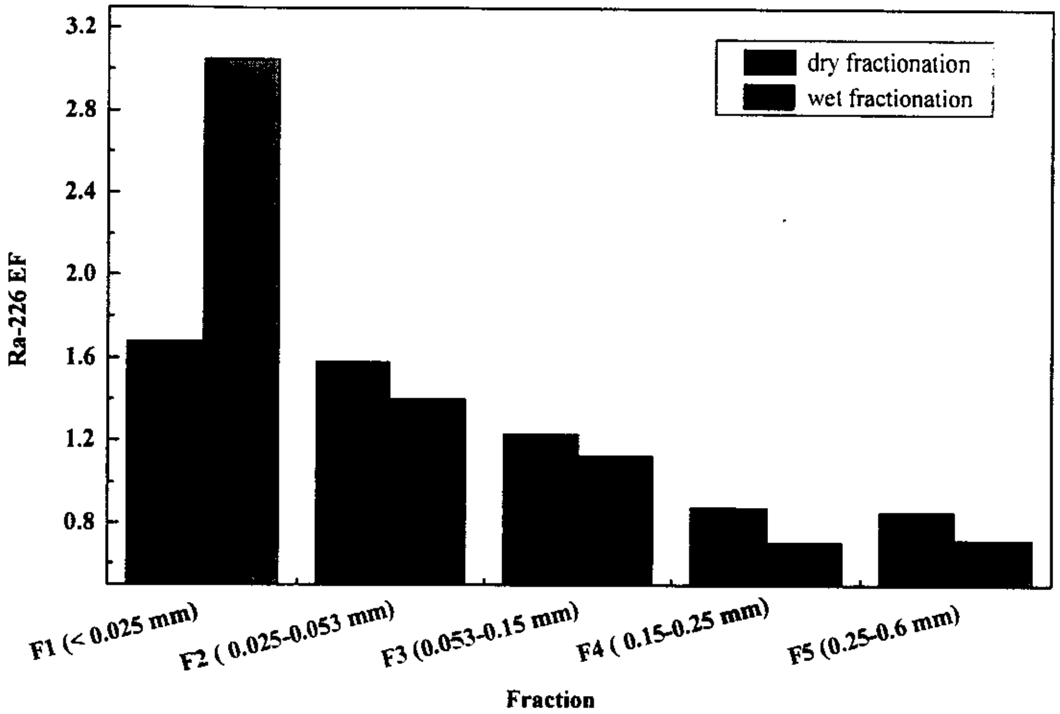

Fig. (3.4): Distribution of Ra-226 enrichment factors with dry and wet sieving fractionation of the PG wastes.

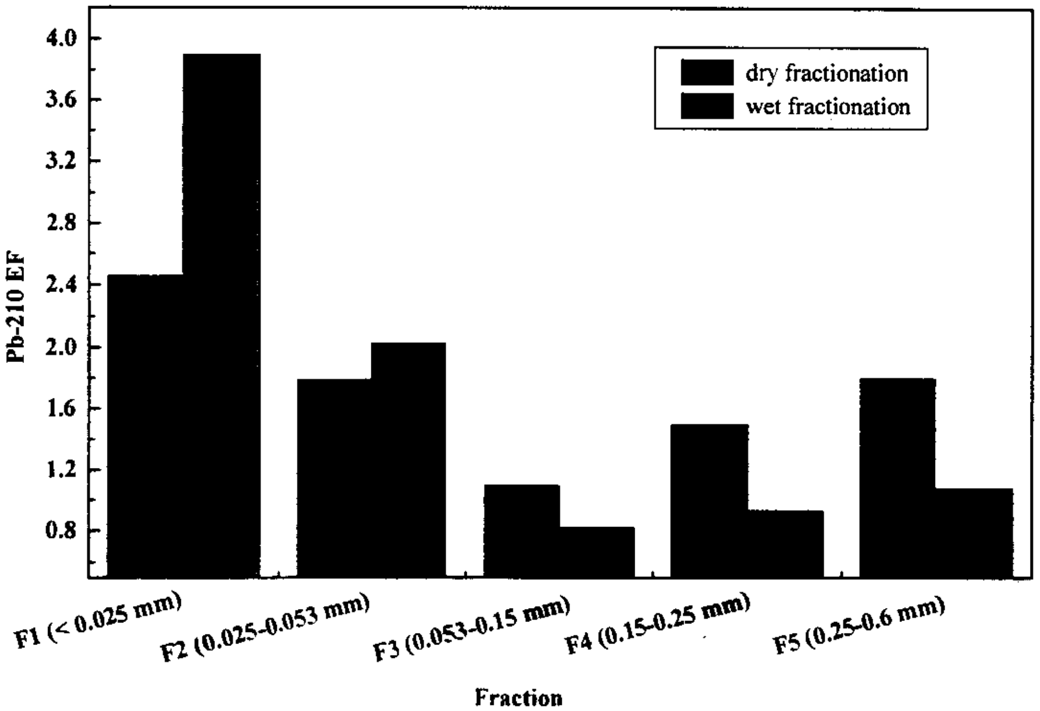

Fig. (3.5): Distribution of Pb-210 enrichment factors with dry and wet sieving fractionation of the PG wastes.

Table (3.14): Elemental analysis of the PG waste using XRF system. *

Element	Compound	Concentration, %
Na	Na_2O	0.49
Al	Al_2O_3	0.23
Si	SiO_2	5.53
P	P_2O_5	2.05
S	SO_3	53.2
Ca	CaO	38.4
Fe	Fe_2O_3	0.001
Sr	SrO	0.081

(*) This analysis is according to the standard used (Semi Q).

3.1.2.2.3. IR spectrometry:

The IR spectra of the PG waste has been measured as potassium bromide (KBr) disc, Fig. (3.7). The spectra show that there are many vibrational absorption bands, characterized mainly to inorganic sulphur compounds [117]. In this concern, the strong absorption band at ~ 1125 cm^{-1} is characterized to stretching vibrations of S=O related to sulphate group as calcium sulphate content in PG waste sample. This band was confirmed by the appearance of another band at 1012 cm^{-1}. Also, there is a strong absorption band at ~ 3613 cm^{-1}, which is attributed to stretching vibrations of Si-OH group, and is confirmed by another band at ~ 795 cm^{-1}. The absorption bands at ~ 3562, 1620 cm^{-1} are related to OH group of water (as moisture) content in PG wastes [118,119]. The absorption bands at 2377, 2315, 2222 and 2140 cm^{-1} are attributed to P-OH stretching of the phosphoric acid residue in PG wastes. The vibrations at 662, 600 and 466 cm^{-1} are due to M-O band which is related to the presence of metal-oxides content in PG waste [117].

3.1.2.3. Radiation hazard indices:

The data obtained in the aforementioned section showed that the most commonly radionuclides in PG waste is Ra-226 and its decay products and low activity levels of Th-232 and K-40. Radon (Rn-222) is one of the daughters in the natural decay series of U-238, and its decay products are (Pb-210, Bi-210 and Po-210). Therefore, the internal exposure due to radon and its radioactive daughters present in the samples under study, produce a large contribution to the average effective dose received by human beings [40]. Therefore, it is important to measure the radon levels directly or from the γ -ray emitting from its daughters in the investigated PG waste samples. The activity concentrations were calculated in PG wastes to determine the different radiation indices, which include, radon emanation fraction (Rn-222 EF), radium equivalent activity (Ra-eq), and absorbed γ -dose rate. The different radiation indices are calculated and discussed below.

3.1.2.3.1. Radon emanation fraction:

The radon emanation fraction (Rn-222 EF) is a very important radiological index used to evaluate the amount of the Rn-222 emanated fraction released from the PG waste materials containing enhanced activity concentrations of

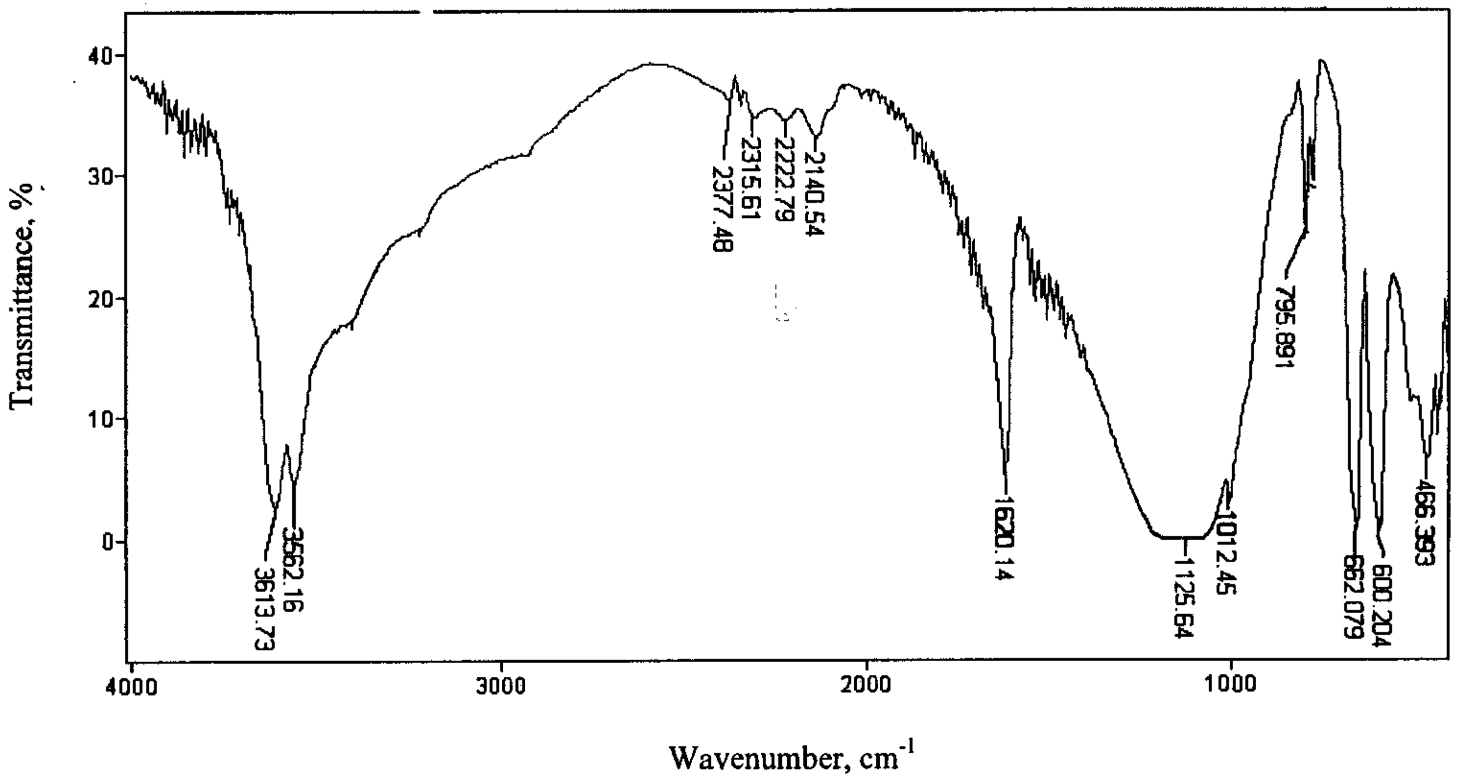

Fig. (3.7): IR –spectra of PG waste sample.

Ra-226. In this study, the assessment of Rn EF is related only to Rn-222 decayed from its parent Ra-226 content in the PG wastes. Since Rn-222 and its respective decay progenies (e.g. Pb-210, Bi-210 and Po-210) have longer half lives than that of other radon isotopes (i.e., Rn-220 or Rn-219), therefore, Rn-222 is considered to be more radiological hazardous to human health than radionuclides coming from other radon isotopes.

In this concern, the Rn-222 EF which is released from the surface of the PG wastes was determined through two measurements by γ -ray spectrometry. The obtained results are presented in Table (3.15). The amount of the Rn-222 EF from the PG wastes is ranged from 18 to 25 % with average value of 22 %. This value is relatively high comparable to the natural value released from soil, wastes associated with oil and gas production, phosphate fertilizer or those reported by others in PG wastes, Table (3.16) [20,92,120-123]. Therefore, it is necessary to find a suitable route to decrease and/or redistribute the radionuclides of the environmental interest (i.e., Ra-226), in PG wastes, consequently to reduce its radiation impacts.

The approaches to the treatment of the PG wastes containing an enhanced activity level of Ra-226 are carried out using physical and/or chemical treatments. These will be discussed later.

3.1.2.3.2. Radium equivalent activity (Ra-eq):

To represent the activity levels of Ra-226, Th-232 and K-40 by a single quantity, which takes into account the radiation hazards associated with them, a common radiological index has been introduced. This index is called radium equivalent (Ra-eq) activity and is mathematically calculated according to the following formula [124]:

$$\text{Ra-eq (Bq/kg)} = A_{Ra} + 1.43\ A_{Th} + 0.077\ A_{K} \qquad (3.1)$$

Where: A_{Ra}, A_{Th} and A_{K} are the activities (Bq/kg) of Ra-226, Th-232 series and K-40, respectively.

Table (3.15): Amount of Rn-222 emanation fraction (%) released from some selected PG wastes.

Sample code	Rn-222 EF (%)
PG-1	25±3
PG-2	23±2
PG-3	21±1
PG-4	23±2
PG-5	22±2
PG-6	18±1
PG-7	22±2
PG-8	19±1
PG-9	25±2
Range	18-25
Mean	22
SD (±)	2.2

Table (3.16): Reported values of Rn-222 emanation fraction released from different resources.

Sample	Location	Rn-222 EF (%)	Reference
PG waste	--	15	[20]
PG waste	--	20.0	[120]
PG waste	Greece	20.1	[92]
PG waste	Austria	29.5	[121]
Phosphate fertilizer	Greece	7.0	[92]
Oil and gas wastes:			
1	Oklahoma	8.7	[122]
2	Michigan	13.8	[122]
3	Texas	3.7	[122]
4	Egypt	6.6	[123]
Soil	USA	9-20	[122]
Sand	Austria	5.9	[121]
PG waste	Egypt	22	The present work

The radium equivalent activity (Ra-eq) is a radiation index, used to evaluate the actual radioactivity in the materials containing naturally occurring 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. (3.1) and are given in Table (3.17). The results obtained showed that the average value of Ra-eq in PG wastes samples is ~ 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 the safe uses in several civil purposes [124,125].

3.1.2.3.3. Total absorbed dose rate ($D_{\gamma r}$):

The absorbed dose rates ($D_{\gamma r}$) due to γ -radiations in air at 1m 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 [112,113]. The conversion factors used to compute the absorbed γ dose rate ($D_{\gamma r}$) in air per unit of activity concentration in Bq/kg (dry weight) corresponds to 0.462 nGy/h for Ra-226 (of U-series), were found to be 0.621 nGy/h for Th-232 and 0.0417 nGy/h for K-40. Therefore, $D_{\gamma r}$ can be calculated according to [113]:

$$D_{\gamma r}\,(\text{nGy/h}) = 0.462\ A_{Ra} + 0.621\ A_{Th} + 0.0417\ A_K \qquad (3.2)$$

The total absorbed dose rate due to γ -emissions was calculated from Eq. (3.2) and the obtained values are presented in Table (3.17). It is obvious that the calculated total absorbed dose rates for some selected samples of PG wastes are ranged from 165 to 268 nGy/h, and the average value was found ~ 207 nGy/h. It is clear that, the total absorbed dose rates increase with the activity concentration, consequently enhances the radiological environmental impacts to the surrounded by the PG wastes. It is recommended that the acceptable total absorbed dose rate established by UNSCEAR [112] must not exceed 55 nGy/h for the workers in areas containing γ -radiations from U-238, Th-232 series and their respective decay progenies, as well as K-40. The obtained results indicated that, the total absorbed dose rates from PG wastes samples under investigation are high by ~ 4-folds relative to the acceptable recommended dose level (i.e., 55 nG/h).

Table (3.17): The radium equivalent activity (Ra-eq index) and absorbed γ -dose rate ($D_{\gamma r}$) calculated for different PG waste samples.

Sample	Ra-eq (Bq/kg)[a]	$D_{\gamma r}$ (nGy/h)[b]
PG-1	373	172
PG-2	368	170
PG-3	400	184
PG-4	355	165
PG-5	404	187
PG-6	425	196
PG-7	379	175
PG-8	517	239
PG-9	500	232
PG-10	504	233
PG-11	578	268
PG-12	559	258
Range	355-578	165-268
Mean	466.7	206.6
SD (±)	76.3	35.4

a: permissible levels of Ra-eq index is 370 Bq/kg [124,125].
b: average worldwide value of $D_{\gamma r}$ is 55 nG/h [112].

3.2. Treatment of the PG Waste:

The PG wastes should be treated to reduce its activity to acceptable levels before its uses in agriculture, road construction and/or additives in cement as building materials. In this concern, the treatment process was carried out based on leaching of the solid PG wastes using different solutions. The dried PG was ground and the homogenized fractions < 0.6 mm (represents 91.3 %) was chosen to perform the treatment process. Different solutions were tried for the leachability process. Distilled water was first used as a leachant solution and the different factors affecting the leaching process were investigated. In addition, other different solutions were tried as leachants such as some mineral or organic acids and salts or a mixture of both acid and its correspondence salts. Also, PG solid waste was subjected to washing and pre-treatment process before the treatment process. Successive processes were also carried out for optimizing the leachability process.

3.2.1. Optimization of Leaching Process:

The leaching conditions required for PG treatment are optimized. In this concern, some factors that affect the leachability before the treatment process for the PG wastes have been studied using distilled water as leachant. The optimization process includes the factors: volume of leachant, contact time, pH and temperature changes.

3.2.1.1. Effect of leachant volume:

Suitable amounts of homogenized PG waste (25 g) were leached using various volumes of distilled water ranged between 25 to 250 ml. The mixture was shaken for one hour at room temperature (25 ± 1 °C), the pH of the distilled water was adjusted to 7 ± 0.01.

The obtained results of the leachability percent of Ra-226 are plotted against the different volumes used of distilled water, Fig. (3.8). It is observed that there is a general increase in the leachability of Ra-226 from the PG waste with increasing the volume of leachant till about 50 ml, to reach a constant leaching percent of Ra-226 (20 %). Therefore, 50 ml of leachant was chosen as a suitable volume for treatment of 25 g of PG waste, i.e., v/m = 2 ml/g.

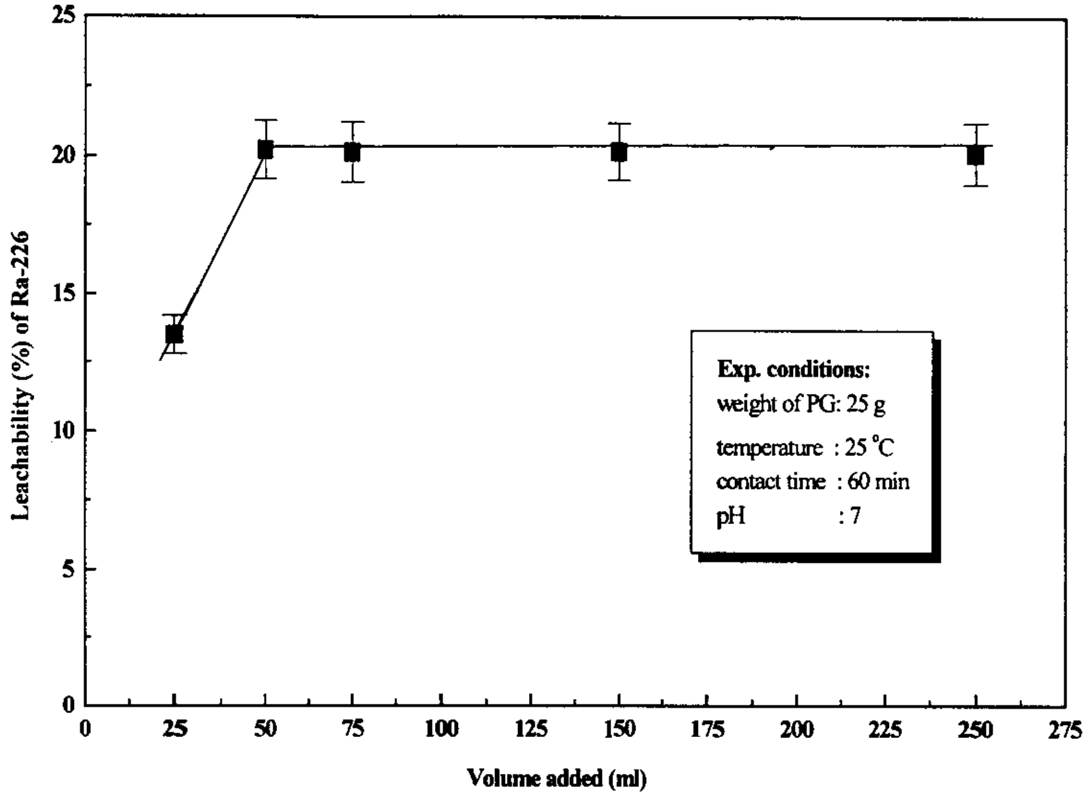

Fig. (3.8): Effect of distilled water volume on the leachability of Ra-226 content in PG waste.

3.2.1.2. Effect of contact time:

The effect of contact time on the removal percent of Ra-226 from the PG waste was investigated. The contact times ranged between 15 to 240 minutes were chosen to study the effect of contact time on the leachability percent of Ra-226 content in the PG wastes. In this concern, 50 g of the homogenized (< 0.6 mm) solid PG wastes was shaken at room temperature (25±1 °C) with 100 ml of distilled water (i.e., v/m = 2), and adjusted to pH 7 ± 0.01. Fig. (3.9) represents the relation between the obtained leaching percent of Ra-226 versus the contact time intervals (min.).

It is clear that there is a general increase of the leachability percent of Ra-226 in the PG waste through the first 60 minutes, followed by a slight decrease of the leachability. The maximum leachability percent of Ra-226 obtained is ~ 20 % in case of leaching using distilled water as leachant. Based on this result, a contact time of 60 minute was chosen as a suitable sufficient contact time for Ra-226 leaching.

3.2.1.3. Effect of hydrogen ion concentration (pH):

This experiment was carried out to study the effect of the acidic and basic media (pH 2-11) of the distilled water on the removal of Ra-226 content in PG wastes. The homogenized PG waste samples (50 g) were leached using 100 ml of distilled water adjusted at various pH's cover the range 2-11 with standard error of 0.01. The samples were shaken for one hour at room temperature (25±1 °C).

The obtained results are presented in Fig. (3.10), as a relation between the leaching percent of Ra-226 present in the investigated PG waste versus the different pH values of the distilled water used. The figure shows rapid increase in the removal % of Ra with pH till ~7. After pH 7, there is no effect on the removal % of Ra-226 at pH more than 7, (i.e. reach a constant removal percent of Ra-226 (~ 20 %) at pH ~ 7). Therefore, the pH ~ 7 is chosen as a suitable pH for leaching Ra-226 from the PG wastes.

3.2.1.4. Effect of temperature:

Samples of 50 g of the homogenized PG (< 0.6 mm) were mixed with 100 ml of distilled water at pH ~ 7. The mixtures were shaken for 60 min at different temperatures ranged between 5 to 80 °C, to investigate the effect of temperature on the leachability percent of Ra-226 from PG waste.

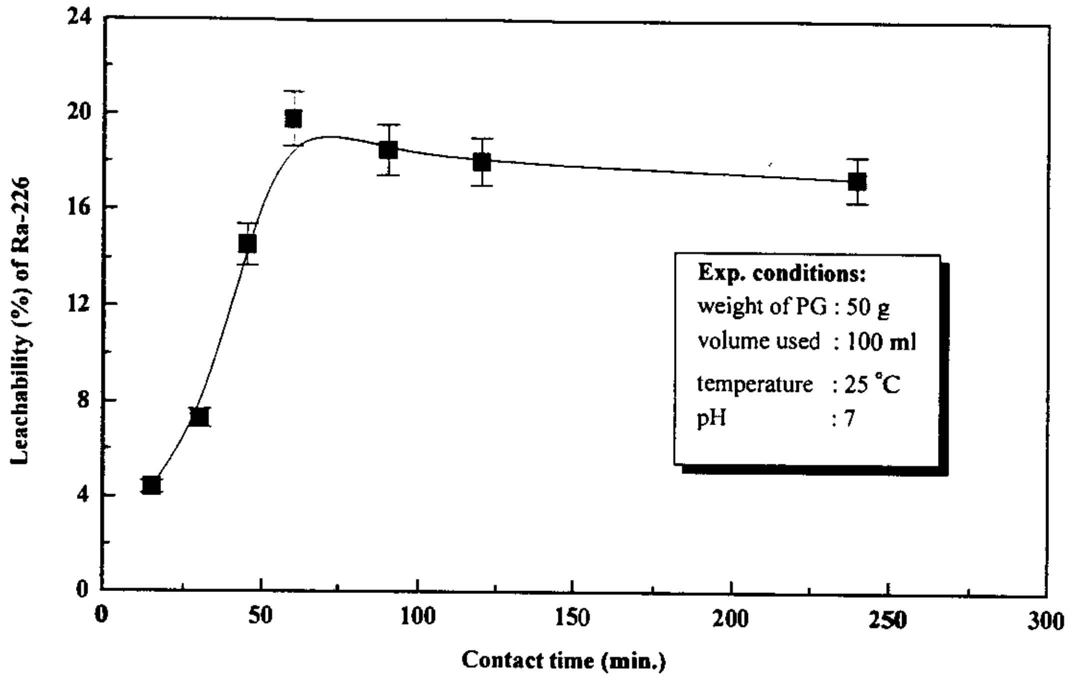

Fig. (3.9): Effect of contact time on the leachability of Ra-226 content in PG waste.

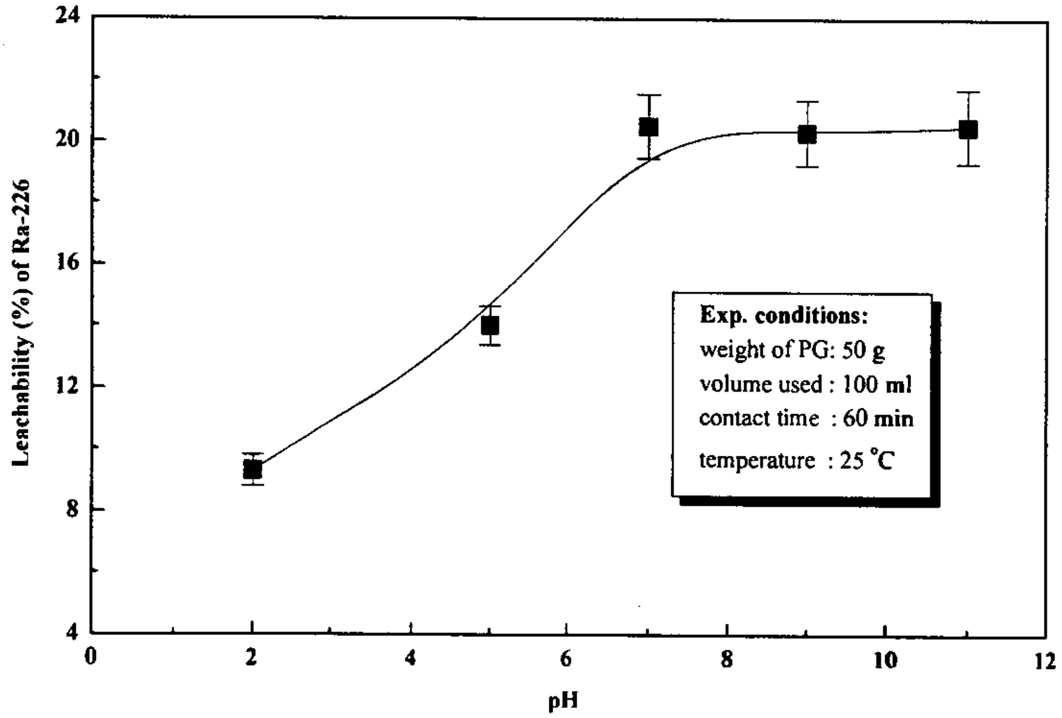

Fig. (3.10): Effect of pH on the leachability of Ra-226 content in PG waste.

The obtained results were plotted between the leachability percent of Ra-226 and temperature, Fig. (3.11). It is clear that the leachability percent of Ra-226 increased with temperature till ~ 25 °C, after which it remains constant till 85 °C. The result indicated that the maximum leachability of Ra-226 was found ~ 20 % at temperature of 25 °C. Therefore, the temperature 25 °C was chosen as optimum temperature to give the maximum leachability percent of Ra-226 content in the PG wastes using distilled water.

Based on all the obtained results, the optimum conditions required for the treatment of Ra-226 in PG wastes with distilled water are given in Table (3.18). It can be concluded that, the ratio between volume of leachant and the weight of PG solid waste is stated by a factor of 2, (i.e., v/m = 2 ml/g). The optimum contact time, pH and temperature are 60 min, ~ 7±0.01 and 25±1 °C, respectively for the homogenized PG (particle size < 0.6 mm), Table (3.18).

Distilled water was used to leaching Ra-226 from PG waste under the optimum conditions, through successive leaching processes. The results indicated that the total removal of Ra-226 content in PG wastes reached 27.8 % through two successive processes.

According to literature related to treatment of PG wastes containing Ra-226, the available data reported in some regions is limited and compared with those obtained in the present work. The total removal of Ra-226 obtained in this study was 27.8 %. This value is comparable with that reported by Haridasan et al. (2002) [19]. They found that ~ 24 % of Ra-226 was removed from PG waste after 10-successive leaching processes [19]. The obtained value in this study is higher than the reported value by Azouazi et al. (2001), where the leached percent obtained is 6 % for Ra-226 from the pretreated PG (calcinated at 800 °C and crushed) [77]. Paul et al. (1984) found that, the total activity of Ra-226 leached out was found 16 %, in case of continuous leaching using PG packed into column and treated with distilled water [78].

3.2.2. Leaching Using Different Acids Solutions:

In this concern, different acids include mineral acids, and some organic acids were used as leachant reagents to reduce the radioactivity concentration of Ra-226 in the PG wastes. The solid waste of PG containing Ra-226 was leached using certain acids of different molar concentrations, under the experimental conditions optimized previously (v/m = 2 ml/g, contact time = 60 min, temperature = 25 °C, and pH = 7).

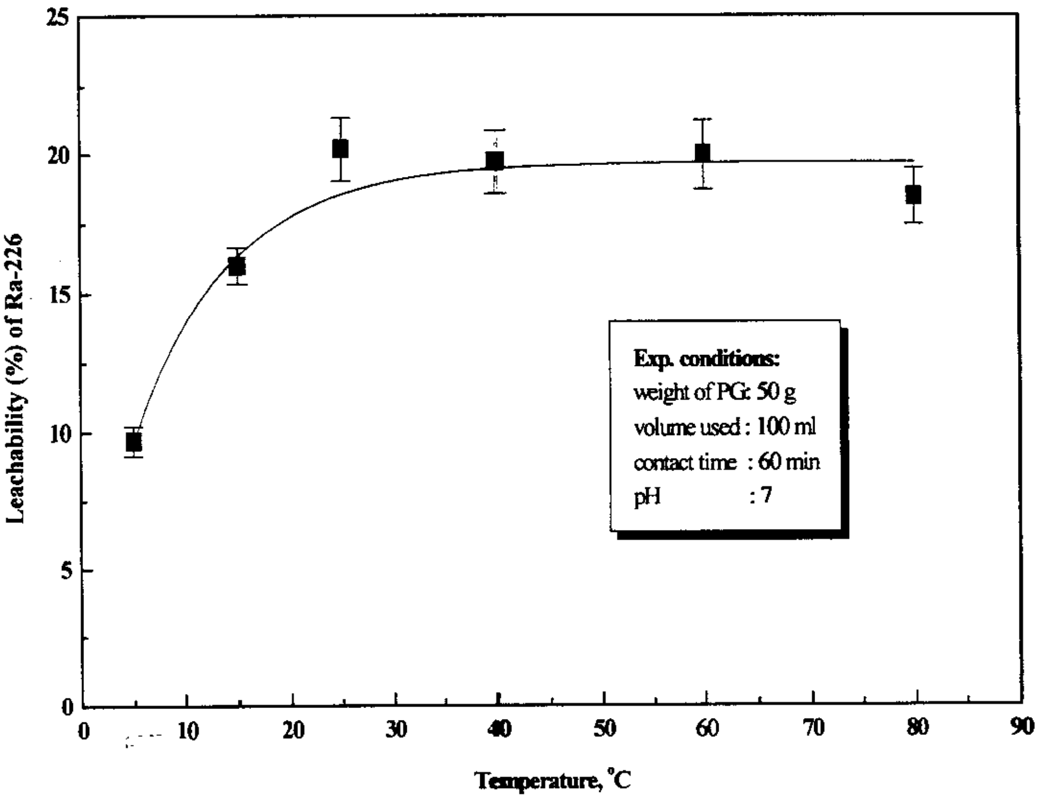

Fig. (3.11): Effect of temperature on the leachability of Ra-226 content in PG waste.

Table (3.18): The optimum conditions for the maximum leachability (%) of Ra-226 in PG wastes using distilled water.

Parameters	Optimum value
Solution/PG waste	2 ml/g
Contact time	60 minute
pH	7±0.01
Temperature	25±1 °C

3.2.2.1. Mineral acids solutions:

Different concentrations of hydrochloric and nitric acids were prepared and used as leaching reagents. Different concentrations of hydrochloric acid solution ranged between (0.5-5M) were used to investigate the removal of Ra-226 from PG wastes. Fig. (3.12), shows the relation between the leachability percent of Ra-226 and the different concentrations of hydrochloric acid used to treat PG waste containing Ra-226. The obtained results indicated that the leachability of Ra-226 increases slowly by using diluted solutions of hydrochloric acid till ~ 1M, followed by a rapid increase with increasing acid concentration till about 2.5M. After this concentration, the leaching percent of Ra-226 not effect by increase the concentration of hydrochloric acid. It was observed that the maximum leachability percent of Ra-226 is 12.6 % by using 2.5M of hydrochloric acid.

The obtained results of leaching percent of Ra-226 using hydrochloric acid are considered as a positive result by comparison with that reported by Azouazi et al (2001). It was found that, Ra-226 is not leached using 4M hydrochloric acid [77].

On the other hand, different concentrations of nitric acid solutions ranged between (0.05 to 4M) were chosen to investigate the effect of nitric acid on leachability of Ra-226, Fig. (3.12). It was observed that, the leachability percent increases with increase in concentration of nitric acid till ~ 2.5M. The maximum leachability of Ra-226 from PG wastes was found ~ 40 % at 2.5M of nitric acid solution.

3.2.2.2. Organic acids solutions:

For this purpose, solutions of different concentrations of the used organic acids, which includes: acetic, oxalic and citric acids were used to reduce the activity of Ra-226 in the PG waste sample, under the optimum conditions used before. The obtained results of organic acid used in this investigation are represented in Fig. (3.13).

In this concern, different concentrations (0.05-2M) of acetic acid solutions were used to study their effect on the removal of Ra-226 content in PG wastes. The obtained results are represented in Fig. (3.13), as a relation between the leachability percent of Ra-226 present in the investigated PG wastes versus concentrations of acetic acid solutions.

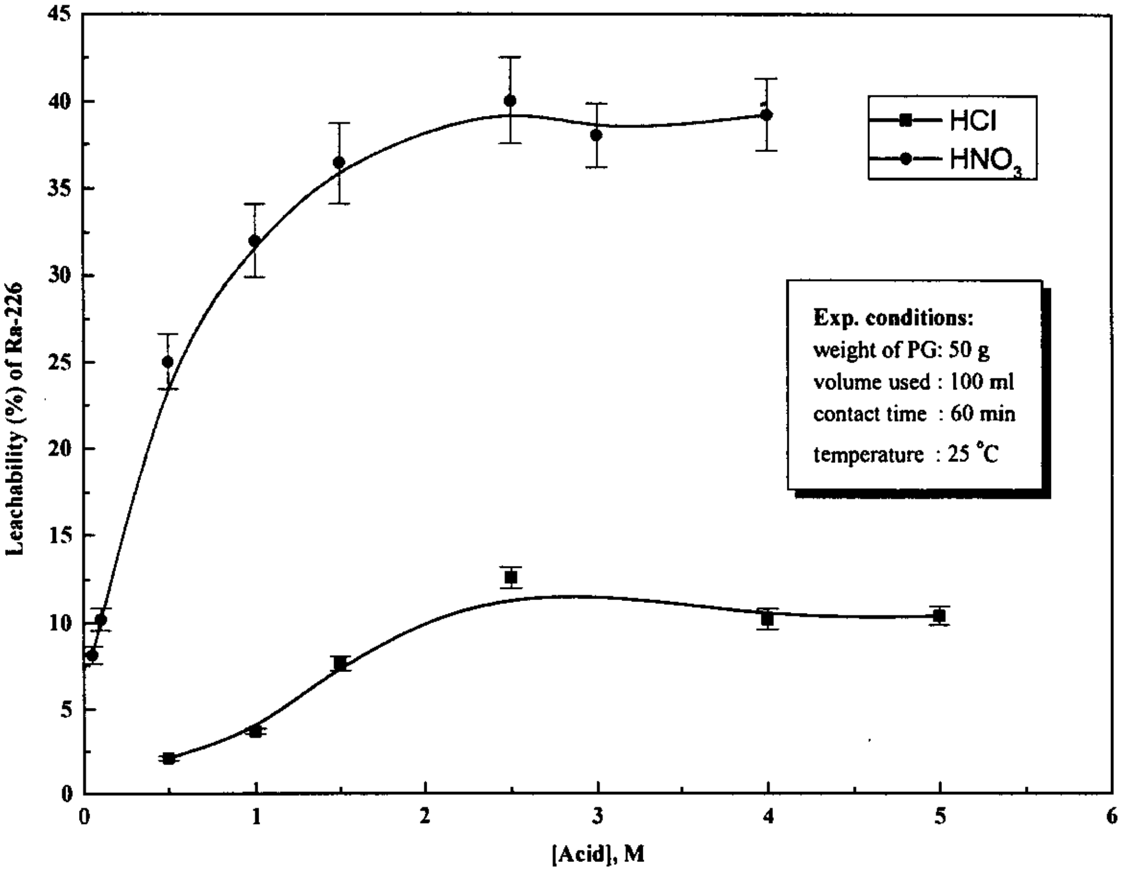

Fig.(3.12): Effect of hydrochloric and nitric acid concentration on the leachability of Ra-226 content in PG waste.

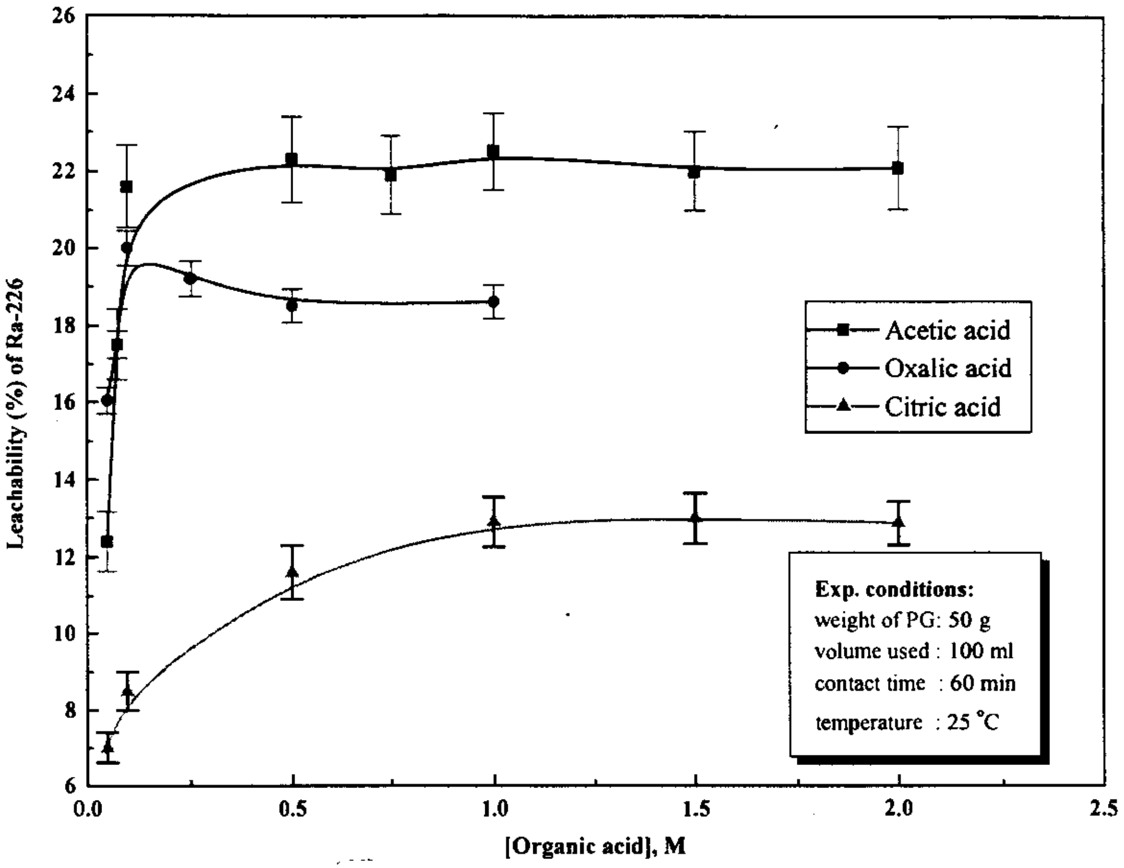

Fig.(3.13): Effect of organic acid concentration on the leachability of Ra-226 content in PG waste.

The obtained results indicated that, the leachability percent of Ra-226 increases with the increase in concentration of the acetic acid solution till about ~ 0.1M, followed by a stability with increases in acetic acid solutions till ~ 2M. The maximum leachability was found ~ 22 % using 0.5M of acetic acid at the optimum conditions.

On the other hand, the effect of oxalic acid concentration on Ra-226 leaching from the PG wastes sample was investigated. Different concentrations ranged from 0.05 to 1M were chosen to perform these experiments. The obtained results are plotted, as a relation between the leaching percent of Ra-226 and concentrations of oxalic acid solutions, Fig. (3.13).

It is observed that, there is a general increase in the leaching percent of Ra-226 content in PG wastes with increasing the concentration of oxalic acid solutions, till 0.1M after which it decreases till 1.0M. The maximum leaching percent of Ra-226 was found 20 % using 0.1M oxalic acid solutions for treatment of PG waste containing Ra-226.

In case of citric acid, different concentrations of citric acid solutions, ranged from 0.05 to 2M were prepared and used as leaching reagents for Ra-226. The obtained results are represented in Fig. (3.13).

The results showed that the leachability of Ra-226 in PG wastes is increased with the concentration of citric acid solutions, till ~ 1M, after which a stability state is obtained. The maximum removed of Ra-226 was found 13 % using 1.5M of citric acid at the optimum conditions.

3.2.3. Leaching Using Solutions of Some Chloride Salts:

For this purpose, some chloride salts of calcium, barium, strontium, and sodium, were used as leachant reagents to study the removal of Ra-226 in PG wastes. The study was performed under the same optimum conditions previously mentioned.

Different concentrations of calcium chloride solutions ranged between (0.05 to 2M) were prepared and used for treatment of PG waste containing Ra-226. Fig. (3.14), shows that the effect of calcium chloride concentration on the removal percent of Ra-226. It is observed that no significant change of the leaching percent of Ra-226 with the concentration of calcium chloride solutions from the range between 0.1 to ~ 0.8M, followed by a gradual increase of the leachability of Ra-226 with concentration more than 0.8M of calcium chloride solution. It is clear that, there is no effect on the removal

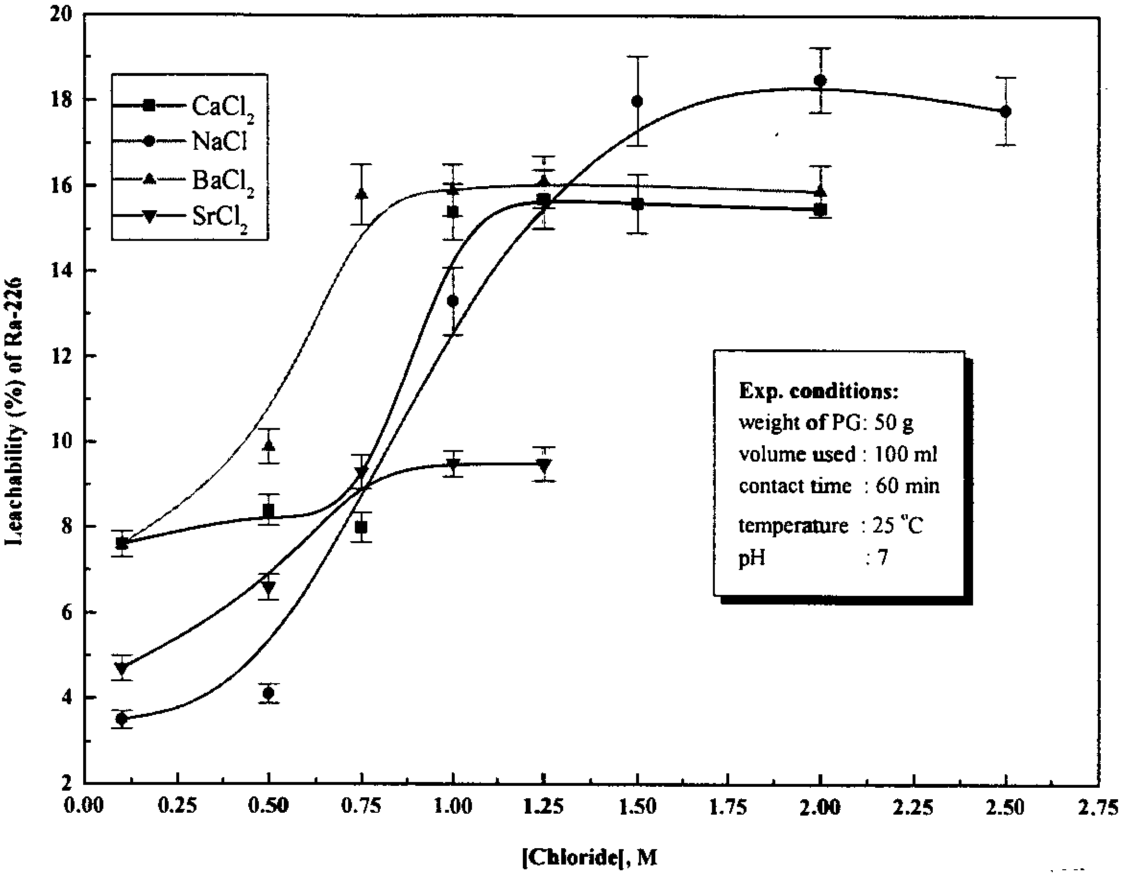

Fig.(3.14): Effect of chloride salts concentration on the leachability of Ra-226 content in PG waste.

percent using calcium chloride solutions more than 1M. The obtained maximum leachability percent of Ra-226 is 15.5 % using 1M of calcium chloride solution at the optimum conditions.

On the other hand, different concentrations of sodium chloride solutions ranged from 0.1 to 2.5M were chosen to show the effect of sodium chloride on the removal percent of Ra-226 from PG wastes. The results are given in Fig. (3.14). It is clear that there is a general increase in the removal percent with increase in the sodium chloride concentrations till 1.5M, after which it reached stability state within concentration range from 1.5 to 2.5M. The obtained maximum leaching percent of Ra-226 is found 18 % using 1.5M of sodium chloride solution.

In case of chloride salts of barium and strontium were chosen to investigate their effect on the removal percent of Ra-226 from the PG waste, Fig. (3.14). The results showed that the leachability percent of Ra-226 was increased gradually with the concentration of barium chloride and strontium chloride solution, to reach a maximum within the concentrations range of 0.75-2M of barium chloride solution and 0.75-1.25M of strontium chloride solution. The results showed that the obtained maximum leaching percent of Ra-226 are 9.5 and ~ 16 % using 1M strontium chloride and 0.75M barium chloride solutions, respectively.

3.2.3.1. Mixed solutions of chloride salts with hydrochloric acid:

The optimum concentration of hydrochloride acid solution and those of chloride salts solution were mixed together as a leaching reagent. The prepared mixture solutions were used to treat the PG waste containing Ra-226. The results obtained are presented in Table (3.19). The results indicated that the leachability percent of Ra-226 from PG wastes was found 10.2, 13.5, 11.7 and 13.6% when using mixtures of 2.5M hydrochloric acid with chloride salts of 1.5M sodium, 1M calcium, and 0.75M strontium and barium chloride, respectively. From the obtained results, the hydrochloric acid and chloride salt mixtures are less efficient comparable to the individual solutions of chloride salts.

Table (3.19): Effect of HCl and chloride salts mixture on treatment of PG waste containing Ra-226.

Mixture*	L, %
2.5 M HCl + 1.5 M NaCl	10.2 ± 0.6
2.5 M HCl + 1.0 M $CaCl_2$	13.5 ± 0.3
2.5 M HCl + 0.75 M $SrCl_2$	11.7 ± 0.5
2.5 M HCl + 0.75 M $BaCl_2$	13.6 ± 0.6

* The mixed solutions were prepared in 100 ml.

3.2.4. Leaching Using Solutions of Some Nitrate Salts:

Solutions of some nitrate salts include, sodium, strontium and calcium nitrate at different concentrations were investigated. These experiments were performed under the optimum conditions. The obtained results are plotted as a relation between leaching percent of Ra-226 with concentrations of nitrate salts solutions, Fig. (3.15).

Different concentrations of sodium nitrate solutions ranged between 0.05 to 2M were used to investigate the removal of Ra-226 from PG waste. The results showed that the leachability percent of Ra-226 was increased gradually with the concentration of sodium nitrate solution, to reach a maximum within the concentrations range of 1-2M of sodium nitrate solution. The maximum leachability of Ra-226 obtained is 20 %.

In case of calcium nitrate, the effect of calcium nitrate solutions concentration on the leachability of Ra-226 content in PG wastes was investigated within concentrations ranged from 0.05 to 2.25M of calcium nitrate, Fig. (3.15). The obtained results indicated that there is a general increase in the leachability percent of Ra-226, with the increase of calcium nitrate solution concentration till 1M, followed by approximate stability of leachability percent till 2.25M. The obtained maximum leachability of Ra-226 in PG wastes was found 48 % from the total activity of Ra-226 within concentration ranged between 2 to 2.25M of calcium nitrate solutions.

On the other hand, Fig. (3.15) shows the effect of strontium nitrate within concentration range from 0.05 to 2M on the leachability percent of Ra-226 present in PG wastes. It is observed that, there is a general increase in the leachability percent of Ra-226 with concentration of strontium nitrate solutions within 0.05-0.5M, followed by stability of the leachability of Ra-226 till 2M. The obtained maximum leachability percent of Ra-226 is 17 % using strontium nitrate solution within concentration range of 0.5-2M, Fig. (3.15).

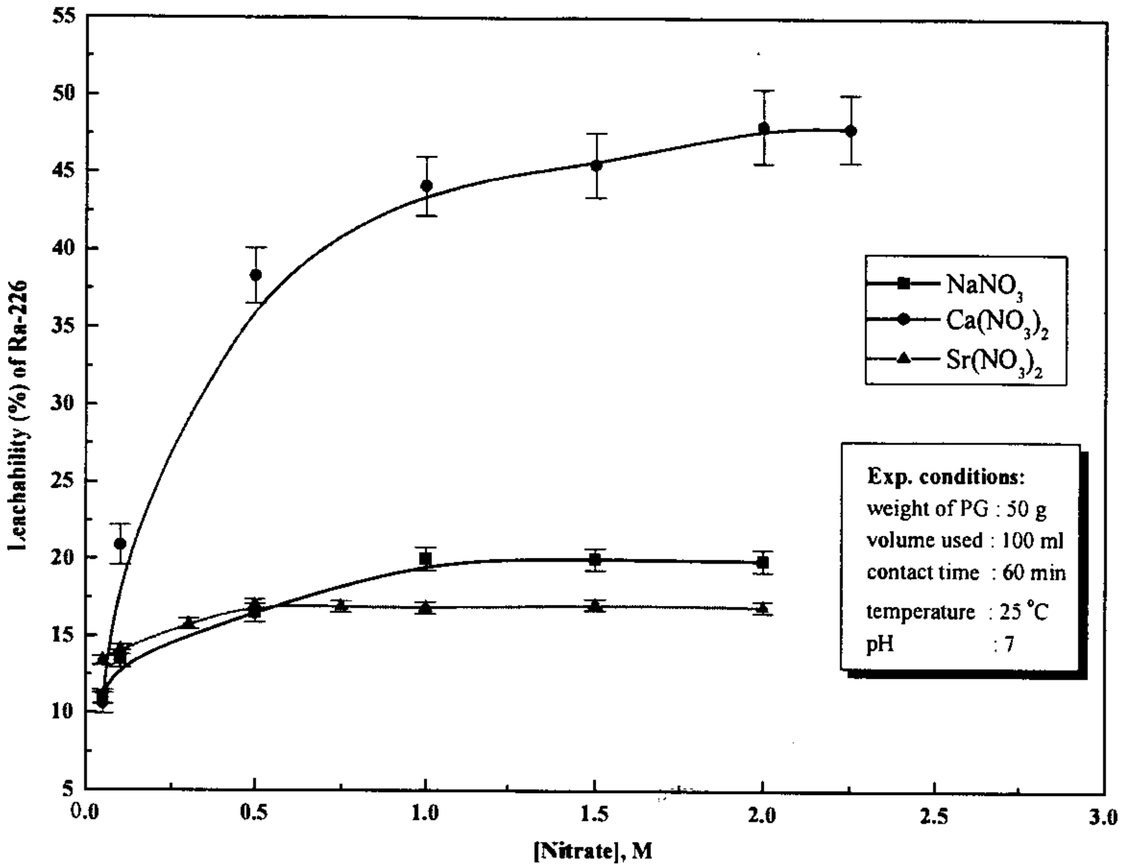

Fig. (3.15): Effect of nitarte salts concentration on the leachability of Ra-226 content in PG waste.

3.2.4.1. Mixed solutions of nitrate salts with nitric acid:

The optimum concentrations of the nitrate salt solutions were mixed with that of nitric acid (i.e., 2.5M). The prepared mixture solution was used to investigate the treatment of the PG wastes to reduce Ra-226 activity. These experiments were performed under the same optimum conditions. The obtained results are listed in Table (3.20).

The results showed that, the leachability percent of Ra-226 are 17.8, 24.6 and 43 % using 2.5M nitric acid solution mixed with nitrate solutions of strontium, sodium and calcium, respectively. These results are nearly in agreement with there obtained from the individual nitrate salts used. This means that addition of nitrate salts to nitric acid solution no enhancement the leachability of Ra-226.

3.2.5. Leaching Using Solutions of Some Organic Salts:

For this purpose, solutions of different acetate, oxalate, and citrate salts of sodium and ammonium of different concentrations were prepared and used as leachant reagents. The obtained data are discussed in the following sections.

3.2.5.1. Solutions of acetate salts:

Acetate salts solutions of sodium and ammonium are used as leaching reagents, at different concentrations ranged between from 0.05 to 2M, for the treatment of the PG waste containing Ra-226.

The effect of sodium acetate concentration on the leachability of Ra-226 in PG wastes was investigated within concentration ranged from 0.05 to 2M. Fig. (3.16) showed the effect of sodium acetate solutions concentration on the leachability percent of Ra-226 in PG wastes. The obtained results indicated that the removal of Ra-226 increased with the concentration of sodium acetate till ~ 0.5M, followed by stability in the leached percent within concentration range of 0.5-2M. The obtained maximum leaching percent of Ra-226 was found 10.5 % using 1.5M of sodium acetate solution under the optimum conditions.

In case of ammonium acetate, the leaching percent of Ra-226 and concentrations ranged from 0.05 to 2M of ammonium acetate solutions, are plotted in Fig. (3.16). The results obtained indicated that there is a slight increase in leachability percent of Ra-226 within the concentrations ranged from 0.05 to 1M of ammonium acetate solutions, followed by a rapid increase

Table (3.20): Effect of HNO_3 and nitrate salts mixture on treatment of PG waste containing Ra-226.

Mixture*	L%
2.5 M HNO_3 + 2 M $Ca(NO_3)_2$	43±2.9
2.5 M HNO_3 + 0.5 M $Sr(NO_3)_2$	17.8±1.5
2.5 M HNO_3 + 1 M $NaNO_3$	24.6±1.1

* The mixed solutions were prepared in 100 ml.

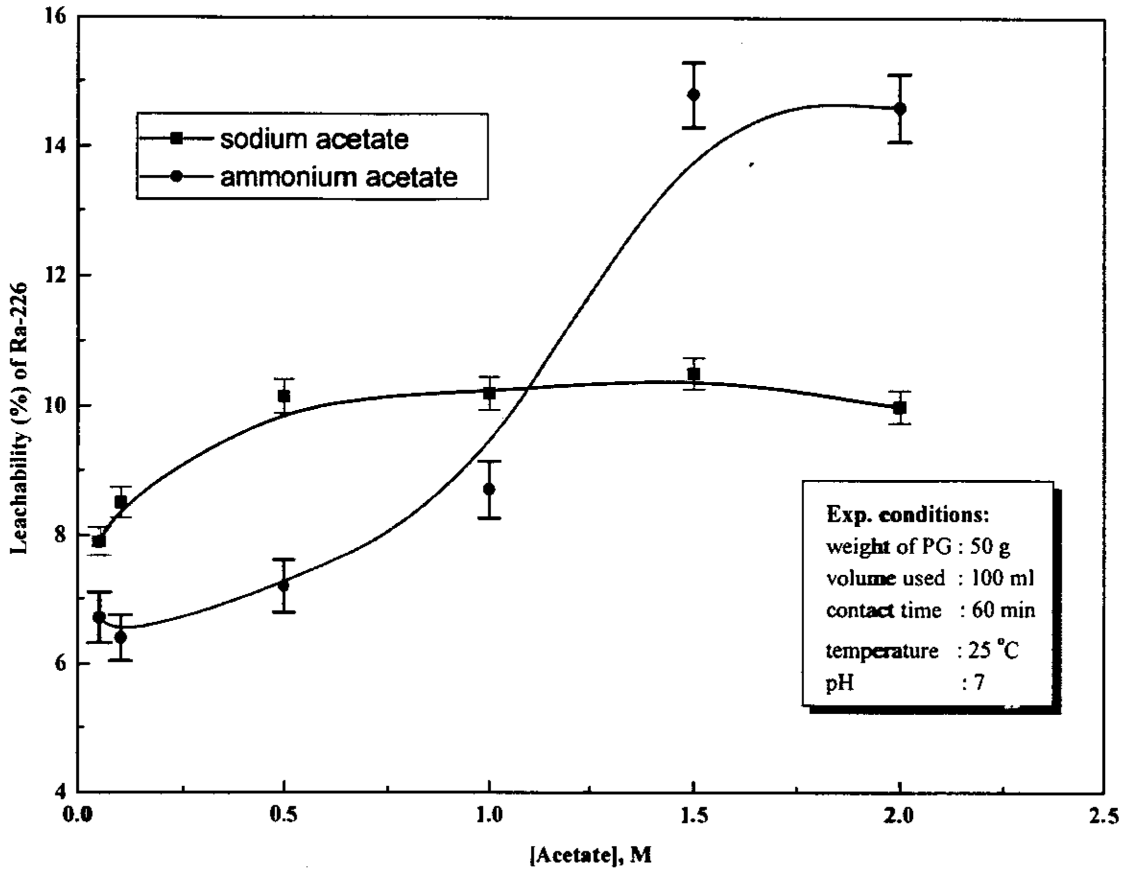

Fig. (3.16): Effect of acetate salts concentration on the leachability of Ra-226 content in PG waste.

from 1 till 1.5M. It is also observed that there is no increase in the leachability percent of Ra-226 with the ammonium acetate solution from 1.5 till 2M. The obtained maximum leachability percent of Ra-226 from PG waste within the stability plateau was found to be 14.8 %.

3.2.5.1.1. Mixed solutions of acetate salts with acetic acid:

Solutions of the optimum acetate salts and acetic acid concentrations were mixed together to be used as leachant reagents for the treatment of PG waste under the suitable experimental conditions. The obtained results are listed in Table (3.21).

The results showed that, the leaching percent of Ra-226 decrease when treating using the mixed acetate salt and acetic acid solutions. The leaching of Ra-226 was found 8.3 % and 7.3 % using 1.5M of sodium and ammonium acetate, respectively, when mixed with 0.5M of acetic acid. From the previous results, it is clear that the acetate salts is not efficient to remove the activity of Ra-226 present in the PG wastes comparable to solution of 1.5 M of ammonium acetate which gives a removal percent of ~ 14.8 %.

3.2.5.2. Solutions of oxalate salts:

Solutions of some oxalate salts include, sodium and ammonium oxalate at different concentrations were prepared and mixed with the PG wastes. These experiments were performed under the optimum conditions previously mentioned.

Different concentrations of sodium oxalate ranged from 0.01 to 0.2M were chosen to investigate the removal percent of Ra-226 content in PG wastes. Fig. (3.17) shows the effect of sodium oxalate solutions concentration on the leachability of Ra-226 from PG waste. The obtained results showed that there is a general increase of the leachability percent of Ra-226 with concentrations of sodium oxalate solutions till 0.1M, followed by stability in the leached percent within concentration range of 0.1-0.2M. The obtained maximum leachability of Ra-226 is 13.8 % using 0.1M of sodium oxalate.

On the other hand, concentrations ranged between 0.05-0.5M of ammonium oxalates were chosen to show their effect on the treatment of PG wastes containing Ra-226. The obtained results are plotted as a relation between the leaching percent of Ra-226 and concentrations of ammonium oxalate solution, Fig. (3.17).

Table (3.21): Effect of mixed acetic acid and acetate salts solutions on the treatment of PG waste containing Ra-226.

Mixture*	L, %
0.5 M acetic acid + 1.5 M sodium acetate	8.3 ± 0.4
0.5 M acetic acid + 1.5 M ammonium acetate	7.3 ± 0.4

* The mixed solution was prepared in 100 ml.

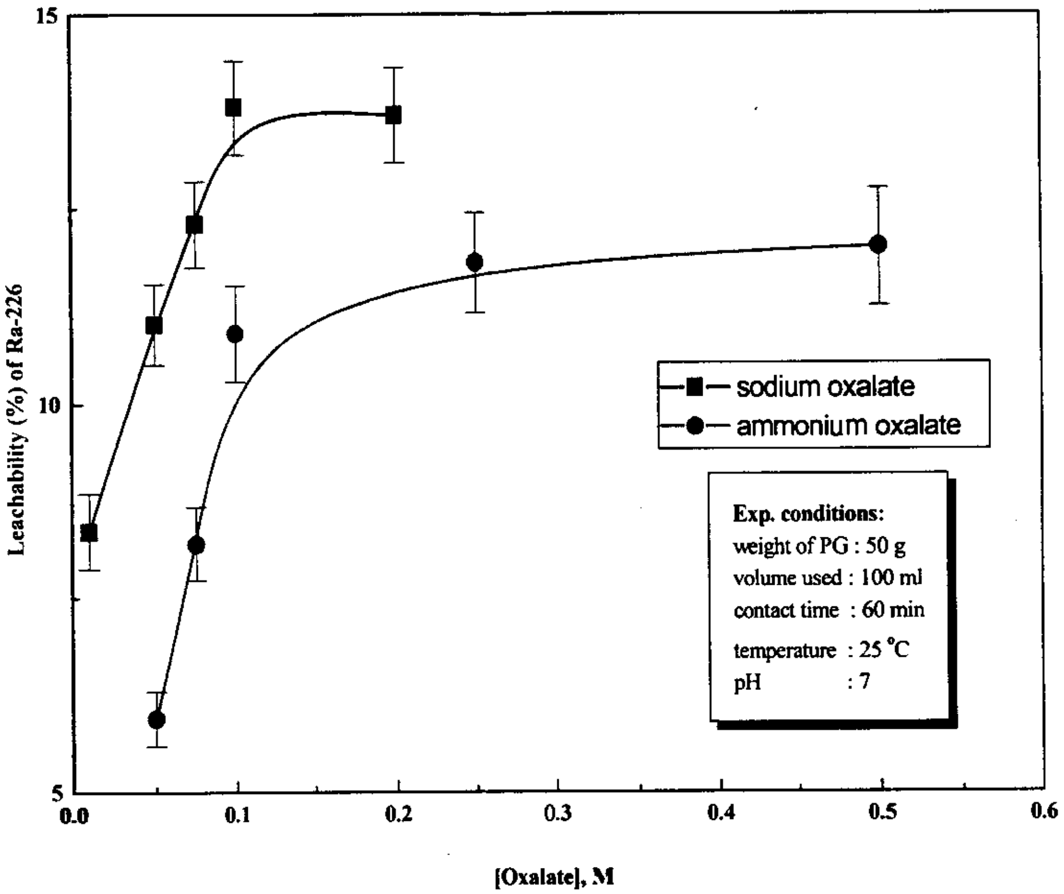

Fig.(3.17): Effect of oxalate salts concentration on the leachability of Ra-226 content in PG waste.

The results indicated that, the leachability percent of Ra-226 increases rapidly with the concentrations of ammonium oxalate solutions till 0.15M, followed by stability within concentrations range of more than 0.15M till 0.5M. The obtained maximum leachability of Ra-226 was found ~ 12 % from the total activity of Ra-226 content in PG wastes.

3.2.5.2.1. Mixed solutions of some oxalate salts with oxalic acid:

In this concern, the optimum solutions concentration of oxalate salts and oxalic acid were mixed together to be used as leachant reagents for the treatment of PG waste under the experimental conditions. The results obtained are represented in Table (3.22). The results indicated that, the leachability percent of Ra-226 in PG wastes was found 12.7 and 12.6 % when treating using solutions of 0.1M oxalic acid mixed with 0.1M of sodium oxalate and 0.25M of ammonium oxalate, respectively. It is observed that, the leachability percent of Ra-226 decreases comparable to that obtained when PG waste was treated using 0.1M oxalic acid alone.

3.2.5.3. Sodium citrate solutions:

Different concentrations of sodium citrate solutions ranged from 0.05 to 1.5M were chosen to investigate the effect of sodium citrate on the leaching of Ra-226 content in PG wastes. The obtained results are plotted as a relation between leachability percent of Ra-226 versus concentration of sodium citrate solutions, Fig. (3.18).

The results indicated that the leaching percent of Ra-226 increases with the concentration increase of sodium citrate solution till 0.5M, followed by slight decrease or nearly stability with increase of sodium citrate solution till 1.5M. The obtained maximum leachability of Ra-226 from the PG waste was found 12.5 % using 0.5M sodium citrate solutions under the optimum conditions.

3.2.5.3.1. Mixed solutions of sodium citrate with citric acid:

In this concern, the optimum concentrations of citric acid (1.5M) were mixed with sodium citrate (0.5M) solution, and used as leachant reagent for Ra-226 from PG waste. The obtained results are listed in Table (3.23). It is observed that, the leachability percent of Ra-226 was found ~ 14.7 %. This value is higher slightly comparable to the leachability percent using sodium citrate solution (0.5M) or 1.5M citric acid solution alone.

Table (3.22): Effect of mixed solutions of some oxalate salts with oxalic acid on the treatment of PG containing Ra-226.

Mixture*	L, %
0.1 M oxalic acid + 0.1 M sodium oxalate	12.7 ± 0.7
0.1 M oxalic acid + 0.25 M ammonium oxalate	12.6 ± 0.7

* The mixed solutions were prepared in 100 ml.

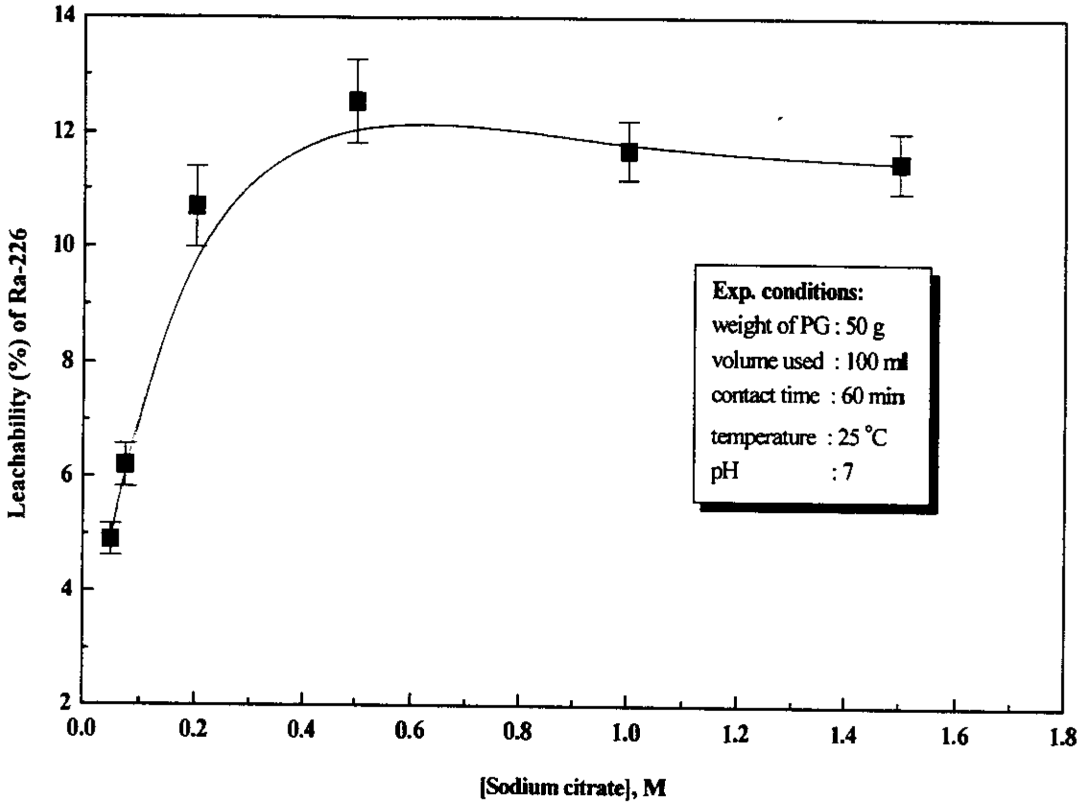

Fig. (3.18): Effect of sodium citrate concentration on the leachability of Ra-226 content in PG waste.

Table (3.23): Effect of mixed solution of sodium citrate and citric acid on the treatment of PG waste containing Ra-226.

Mixture*	L, %
1.5 M citric acid + 0.5 M sodium citrate	14.7 ± 0.9

* The mixed solutions were prepared in 100 ml.

3.2.6. Improvement of the Leachability Process:

Based on the results obtained from the leaching process of Ra-226 from PG solid waste using different solutions, it is clear that both nitric acid solution and a mixture of nitric acid and calcium nitrate solution show the highest values for the leachability percentage. Nitric acid solution was chosen since it is more economic than using the mixture. In a trial to improve the leachability percent using nitric acid as a leachant solution, two different processes were carried out.

3.2.6.1. Successive leaching using solution of nitric acid:

In this concern, 2.5M of nitric acid solution was used to treat the PG waste containing Ra-226 under the same experimental conditions (shaking time 60 minute at 25±1 °C), through successive leaching processes. The obtained results are presented in Table (3.24).

The obtained results showed that, the removal of Ra-226 content in PG waste was found 40.5 % using 2.5M nitric acid solution through the first step. In addition, the removal of 10.8 % was obtained through the second step. It is clear that the treatment of PG waste containing Ra-226 using 2.5M of nitric acid through two successive steps removed more than 51 % of the total Ra-226 present in PG waste.

3.2.6.2. Pre-treatment before using nitric acid as a leachant solution:

Pre-treatment processes were carried out by firstly washing the PG waste (in a trail to decrease its acidity nature), secondly, by pre-treatment using ammonium carbonate solution. In this concern, three samples of PG waste were taken and each was subjected to a washing process using, distilled water, 0.05M of sodium hydroxide or 1 % of sodium carbonate. Then, each of these samples was pre-treated by 20 % of ammonium carbonate solution. In each case, the mixture was shaken for 4 hour at 85 °C, cool down at room temperature and then filtered. The pre-treated PG waste was then treated with 2.5M of nitric acid solution under the same optimum conditions used before, through two successive processes. The obtained results are given in Table (3.25).

Table (3.24): Successive leaching processes of PG waste containing Ra-226 using 2.5M nitric acid solution.

Leaching sequence	Leaching, %
1st. step	40.5±2.4
2nd. step	10.8±0.7
3rd. step	----
Total	51.3±3.1

Table (3.25): Successive leaching processes of pre-treatment of PG waste containing Ra-226 using ammonium carbonates solution (20 %).

Sample code	Washing by	Leaching, %			
		Washing	1st. HNO_3	2nd. HNO_3	Total
PG-1	Distilled water	12.1±0.9	36.6±3.4	9.9±1	58.6±5.3
PG-2	0.05M NaOH	10.9±0.9	45.7±4.9	13.6±1.5	70.2±6.8
PG-3	1 % Na_2CO3	13.4±1	28.7±2.6	24.2±2.5	66.3±6.1

It was found that about 59, 70 and 66 % of Ra-226 were removed when the PG samples were washed with distilled water, 0.05M of sodium hydroxide and 1 % of sodium carbonate solution, respectively. These results were obtained after treating the washed samples with 20% of ammonium carbonate solution, followed by two successive treatment processes with 2.5M of nitric acid solution. Therefore, 0.05M of sodium hydroxide solution was chosen for washing the PG waste sample before treatment in the following experiments.

In a trial to enhance the leachability of Ra-226 from PG waste sample, 20 % sodium carbonate solution was used instead of ammonium carbonate solution after washing the PG sample with 0.05M sodium hydroxide solution. The washed PG waste sample was pre-treated by 20 % of sodium carbonate solution. The mixture was shaken for 4 hour at 85 °C, cool down at room temperature and then filtered. The pre-treated PG waste was then treated with 2.5M of nitric acid solution under the same optimum conditions used before. It was found that ~ 87 % of Ra-226 was leached when using 20 % sodium carbonate solution as a pre-treatment process before using 2.5M nitric acid solution as a leaching reagent after two successive leaching processes. Based on the previous data, the results indicated that the pre-treatment of PG wastes containing Ra-226 by sodium carbonate solution is more efficient than the ammonium carbonate solution. Therefore, sodium carbonate solution was chosen for pre-treatment of PG wastes before treatment by nitric acid solutions in the following experiments.

On the other hand, 20 % of sodium carbonate solution was tried as a pre-treated solution for PG waste sample directly without using 0.05M sodium hydroxide as a washing solution. After that the pre-treated PG waste was leached by 2.5M nitric acid as mentioned before. The obtained results showed that 43 % of Ra-226 was removed from the PG waste. Therefore, it is clear that using 0.05M sodium hydroxide as a washing solution is an essential step before pre-treatment of PG with 20 % sodium carbonate solution, followed by treatment with 2.5M nitric acid.

3.2.6.3. Optimization of the pre-treatment process:

For this purpose, the pre-treatment conditions required for PG treatment are optimized. In this concern, some factors that affect the pre-treatment process for the PG wastes have been studied using 20 % of sodium carbonate solution as leachant. The optimization process includes the factors: contact time, temperature and concentrations of sodium carbonate solutions. These factors are investigated in the following sections.

3.2.6.3.1. Effect of contact time:

The washed PG wastes sample was taken and pre-treated by 20% of sodium carbonate solution. The mixture was shaken at different contact time at 85 °C. The period of 15 minutes to 4 hour was chosen to investigate the effect of contact time on the pre-treatment of PG waste containing Ra-226. Then, the sample was treated again by 2.5M of nitric acid solution.

The obtained results are plotted, as a relation between the total leaching percent of Ra-226 and the respective contact time, Fig. (3.19). It is clear that, there is a general increase in the removal of Ra-226 in the first 2 hour, and no effect of contact time after 2 hour was observed. The total maximum removal of Ra-226 content in the PG waste was found 87 % from the total activity of Ra-226 present in PG waste. Therefore, a contact time of 2 hour was chosen as a suitable sufficient contact time for pre-treatment of PG waste containing Ra-226, to attain the best leachability percent of Ra-226.

3.2.6.3.2. Effect of temperature:

For this purpose, the effect of temperature on the pre-treatment of PG waste was investigated within temperatures ranged from 15 to 85 °C. The washed PG waste sample was mixed with 20 % of sodium carbonate solution for shaking time 2 hour at different temperatures. The pre-treated PG waste sample was treated using 2.5M of nitric acid solution through two successive leaching processes. The obtained results are plotted as a relation between the total leachability percent of Ra-226 and temperature, Fig. (3.20).

The results indicated that the total removal of Ra-226 increased with temperature till 25 °C, after which a plateau is obtained. Therefore, the temperature of 30 °C was chosen as an optimum temperature for pre-treatment of PG waste. The obtained maximum removal of Ra-226 content in PG waste was found 87 % from the total activity of Ra-226 present in PG waste.

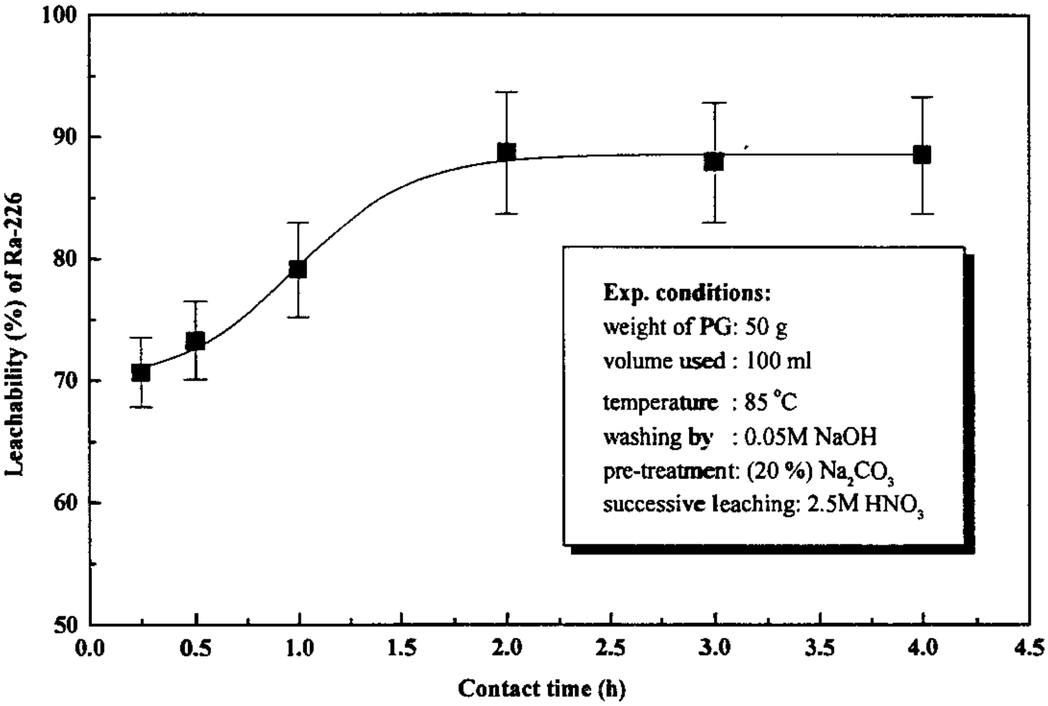

Fig. (3.19): Effect of contact time on the pre-treatment of PG waste containing Ra-226 and the total leachability (%) of Ra-226 using sodium carbonate solution.

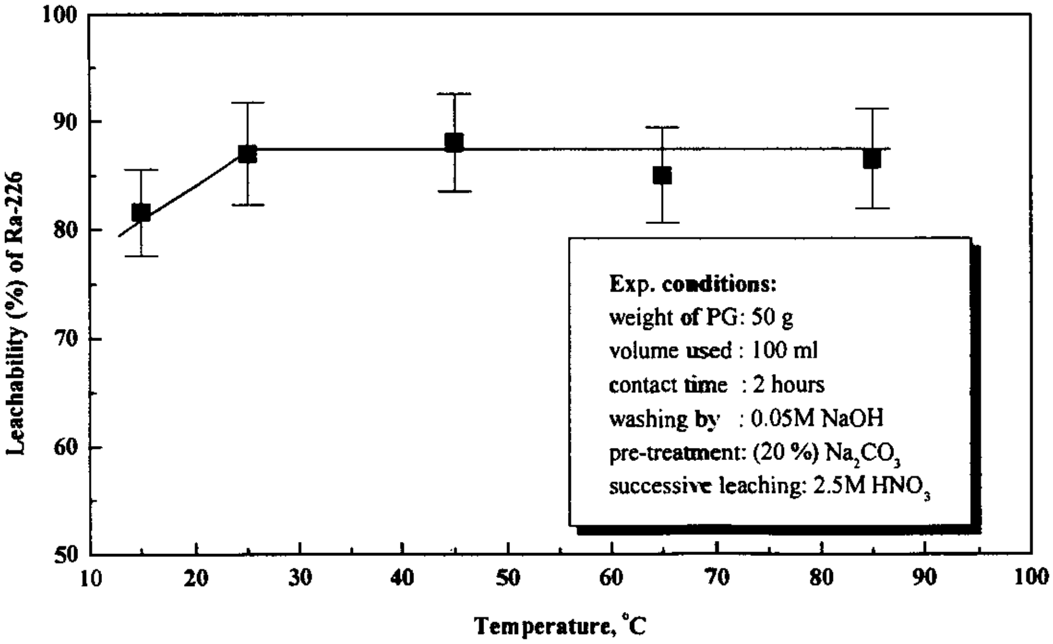

Fig. (3.20): Effect of temperature on pre-treatment of PG waste containing Ra-226 and the total leachability (%) of Ra-226 using sodium carbonate solutions.

3.2.6.3.3. Effect of sodium carbonate concentration:

Different concentrations of sodium carbonate solution were tried as pre-treated solution for PG waste sample after washing the PG waste with 0.05M of sodium hydroxide solution. The concentration of sodium carbonate solution was ranged from 10 to 30 %. The effect of these different concentrations on the leachability percent of Ra-226 when treated with 2.5M nitric acid solution is given in Fig. (3.21).

It is clear that, maximum leaching is given when using 20 % or more of sodium carbonate solution as a pre-treating leaching reagent for PG waste before treated using nitric acid solution. Therefore, 20 % sodium carbonate solution is recommended to be used for pre-treatment of PG waste sample before the leaching process.

3.2.7. Conclusion of Treatment:

Based on the previous results, treatment of PG wastes samples containing Ra-226 using different solutions can be concluded in:

(i) Leaching of the radioactive material (i.e., Ra-226) present in PG wastes is more efficient by using nitric acid solutions compared to hydrochloric acid solutions.

(ii) Mono-carboxylic acid, acetic acid, was found to be more effective for leaching of Ra-226 than other di- or tri-carboxylic acid solutions. This may be due to steric or bulking of di- or tri-carboxylic acid groups when reacted with the atoms of Ra-226. The leachability order of the used organic acids is as follows:

acetic acid > oxalic acid > citric acid

(iii) Leaching percent of Ra-226 using solutions of the chloride salts, showed that leachability order of the used chloride salts is as follows:

$$NaCl > BaCl_2 > CaCl_2 > SrCl_2$$

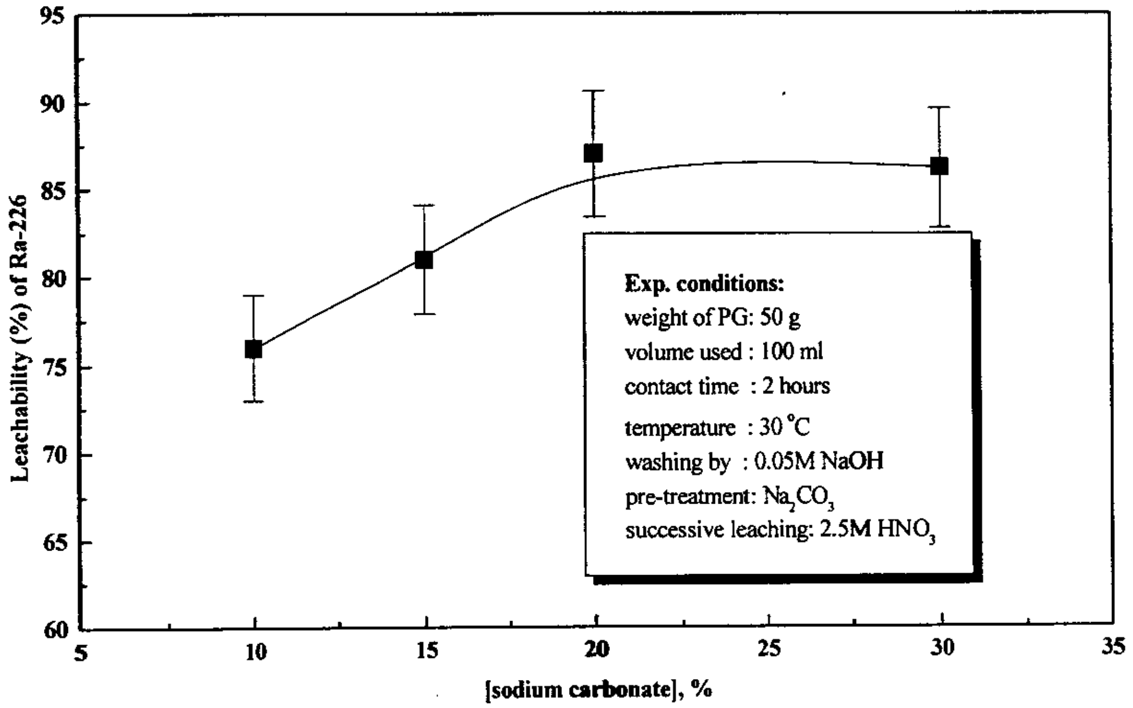

Fig. (3.21): Effect of sodium carbonate concentration on pre-treatment of PG waste containing Ra-226 and the total leachability (%) of Ra-226.

(iv) Leaching using salts of nitrate solutions, showed that the order of the leachability percent of nitrate salts is as follows:

$$Ca(NO_3)_2 > NaNO_3 > Sr(NO_3)_2$$

(v) Using solutions of the different organic salts, the higher leaching percent of Ra-226 was 14.8 % using 1.5M of ammonium acetate solutions compared to the other investigated organic salts.

(vi) Using successive leaching processes, the maximum removal of Ra-226 was found 51 % using nitric acid solutions after two successive processes.

(vii) Using 0.05M sodium hydroxide as a washing solution, followed by 20 % sodium carbonate solution as a pre-treated solution showed the highest leachability percentage when using 2.5M nitric acid solution as a leaching solution.

In conclusion, it is clear that, Ra-226 is very bounded in PG wastes (calcium sulphate). Therefore, 0.05M sodium hydroxide as washing solution, 20 % sodium carbonate solution is recommended to be used for pre-treating PG waste sample before the successive leaching process using 2.5M nitric acid. Fig. (3.22) shows the flow sheet for the recommended process for the leachability of Ra-226 from PG wastes.