Distribution of Radionuclides in the Leachates for Several Rock Types at Different Time Intervals

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Abstract: In the present study, the behavior of the different isotopes activity concentrations for three different rock samples (siltstone, shale and sandy dolomite) as well as in the different leachates of these rocks were studied at different time intervals, using a HP-Ge spectrometer. The activity concentration of ^{238}U for the leachates gradually increases while that for ^{235}U is nearly constant. The results revealed that the solubility gradually decrease from ^{235}U to ^{234}U, ^{238}U and ^{226}Ra respectively. The reason for the higher ^{234}U concentrations in leachates is due to α- recoil process which enhances the mobilization and solubility of the decay product of ^{234}U relative to the parent (^{238}U).Also the ^{238}U activity concentration percent in leachates to that in origin samples increases towards equilibrium state due to the growth of the ^{234}Th. It is noticed that the $^{238}U\%$ of siltstone and shale are very close and higher compared to dolomite which is much less in spite of the higher activity of the dolomite rock sample. The ratio ($^{234}U/^{238}U$) for the first measurement of the leachates was considered at zero time as 1.09±0.17, 1.4±0.21 and 1.6±0.18 for siltstone, shale and sandy dolomite respectively. The enrichment of ^{234}U is accordingly related to the crystal damage and leaching, which are the main mechanisms for the ($^{234}U/^{238}U$) disequilibrium. The variations in the activity ratio ($^{238}U/^{235}U$) are related to the increase in the activity concentration of ^{238}U with time and also to very little variations in ^{235}U.The solubility for Ra, Th, and K are very low and mainly remain in the residuals.

Key Words: Gamma-spectrometry; Leachates of rock types; Uranium activity ratios.

1. Introduction

Uranium, the heaviest naturally occurring element on the earth, plays an important role in daily life because of its use in nuclear power plants. It comprises three natural isotopes (^{234}U, ^{235}U, and ^{238}U) with relative isotopic abundances of 0.0054%, 0.720% and 99.275%, respectively [1]. These values may have small variations depending on the geographic origin of rocks due to natural isotopic fractionation, nuclear reactions or anthropogenic contamination. Precise measurement of the isotopic composition of uranium is of importance for the nuclear industry as well as in environmental and earth sciences. In earth sciences, interest is centered on the observation of the parent/daughter pairs in the U and Th decay series, which are present in natural samples in radioactive equilibrium. In case of environmental sciences, soil and sediments are the most suitable materials that preserve any remains of anthropogenically altered uranium [1].

$^{238}U/^{235}U$ isotope ratio has changed dramatically during earth history from about 3.3 to the present-day value of 137.88 [2, 3and 4].The natural variations, observed on earth today, must have been produced by chemical reactions that fractionate isotopes [5, 6, and 7].

Knowledge of the $^{234}U/^{238}U$ activity ratio in the ecosystem provides information about the mechanisms and processes of uranium transport and origin. It is estimated to be greater than one. Some factors are suggested to influence the uranium isotope ratio; the age of rocks, rock types and climate differences. In rocks older than a few million years, $^{234}U/^{238}U$ activity ratio should be in secular equilibrium [8].

However, the highly energetic alpha-decay of ^{238}U damages a mineral's crystalline lattice and allows ^{234}U to be more mobile during weathering of rocks by meteoric waters. Increased physical weathering and the resulting decrease in grain size increase the mineral surface area (per unit volume). This increases the number of alpha recoil fractures that are exposed to the surface of the grains, which in turn allows for an increased rate of ^{234}U removal [9]. The rate of this removal is expected to decline with time as the more labile uranium is removed first, leaving the less- mobile uranium in the mineral crystalline lattices [10]. Rock type determines rock weathering rates. Where dolomite weather the most rapidly one is followed by shale and sandstones. Climate differences have been hypothesized to affect the $^{234}U/^{238}U$ activity ratio [11, 12].

The separation of radionuclides from any ore material passes through two steps. The first step is the leaching or dissolution of radionuclides by either acid or alkaline solution or then separation (filtration) of the solution (leachate) from the solid (residual).The second step is the precipitation of radionuclides from the leachate.

In the present study, the radionuclides were measured for the original rock samples (shale,

siltstone, and sandy dolomite) and their leachates (solution after leaching processes) by HP-Ge detector at three time intervals starting directly after leaching processes (zero time) to follow-up their radionuclides distribution. Siltstones are usually characterized by strong to very strong radioactivity due to their composition and can be more radioactive than shale. The high radioactivity for sandy dolomite may be due to the presence of phosphate or organic matter[13] Thus, the main aims of this study is to determine the concentration of dissolved ^{234}U, ^{238}U, ^{235}U isotopes and the ratios(^{238}U/^{235}U and ^{234}U/^{238}U) with their possible variations .

2. Samples Preparation

Different rock samples were collected from different sedimentary rocks, at west of WadiNaseib area, Southwestern Sinai, Egypt. 20 rock samples of each type were chosen, crushed and grounded to mesh 60 and then quartered to obtain representative sample of each rock type, they were packed in 200 ml marinelli beakers and sealed for measuring, after 28 days. These samples were prepared for gamma-ray spectrometric analyses by HP-Ge spectrometer.

Leaching processes were carried out on 100 g from each sample, using 30% H_2SO_4 and the leachates were separated (filtered) and packed in 200 ml marinelli and prepared for measuring the activity concentration (Bq/l) for different radionuclides

Gamma-ray Spectrometric Analysis

The gamma spectrometer was used to measure the activity concentrations for the different uranium isotopes in three different rock samples. In addition the behavior of the isotopes concentrations in the different leachates of these rocks was studied at different time intervals.

The work was carried out, using a closed-end coaxial gamma-ray detector (n-type) made of high purity germanium (HP-Ge) in a vertical configuration (Pop- Top cryostat configuration) cooled with liquid nitrogen. The used HP-Ge (EG&G Ortec Model GMX60P4) has a resolution of 1.10 keV at the 5.9 keV gamma transition of ^{55}Fe and 2.3 keV at the 1.33 MeV gamma transition of ^{60}Co. The detector has a photo-peak relative efficiency of about 60 % of the 3" × 3" NaI(Tl) crystal efficiency. The spectrometer has a peak-to-Compton ratio of about 56 to 1 at the 1.33 MeV peak transition of ^{60}Co. Energy calibration of the detector was performed, using standard point sources.

The efficiency calibration was performed by using threewell-known reference materials obtained from the International Atomic Energy Agency for U, Th and K activity measurements: RGK-1, RGU-1 and RGTH-1[14, 15]. The IAEA reference materials are similar to the examined rock samples Absolute efficiency calibration of the gamma spectrometry

system was carried out, using the radionuclide specific efficiency method in order to reduce the uncertainty in gamma-ray intensities, as well as the influence of coincidence summation and self-absorption effects of the emitting gamma photons [16]. The sample containers were placed on top of the detector for counting.

The ^{238}U concentration was determined by 63.3 keV and confirmed by 1001 KeV,then the same geometry and size were used for both the samples and the reference materials [17]. The different concentrations of each rock sample were measured for about one day. The first measurement of the leachates was considered at a time (t = 0) and was measured directly after the leachates were prepared Each leachate was measured for an accumulation time between 2 &3 days and the measurement was repeated at different time intervals to study the behavior of the isotopes concentration with time. An empty cylindrical plastic container (polyethylene marinelli beaker) was measured, for a counting period of 3 days in order to collect the background count rates.

Uranium-238 activity was determined indirectly from the gamma-rays emitted by its daughter products (^{234}Th and ^{234m}Pa) whose activities are determined from the 63.3 and 1001 keV photo-peaks, respectively [18]. The uranium-235 activity was determined directly by its gamma- ray peaks; 143.8, 163.4, 185.7, and 205.3 keV[19, 20, and 21]. The ^{234}U activity was determined directly from the gamma-rays emitted from this nuclide at energy of 53.2 keV[22, 23].

The specific activity of ^{40}K was measured directly by its own gamma-ray at 1460.8 keV. The specific activity of ^{214}Pb was measured, using the 295.2 keV and 351.9 keV, while the specific activity of ^{214}Bi was measured, using the 609.3 keV. The mean specific activity of ^{232}Th was measured, using decay products in secular equilibrium; the 338.4 keV&911.2 keV from ^{228}Ac and 583 keV& 2614.4 keV from ^{208}Tl.

3. Results and Discussions

The activity concentrations of the individual radionuclides were measured for three rock samples and at different time intervals starting directly after the leachates were prepared. The results are presented in Tables 1, 2 and 3. The activity concentration of ^{238}U for the leachates gradually increases from 1143±22.54 to 1971±23.34 Bq/l for siltstone, while that of shale it increases from 1079±21.42 to 1921±30.39 Bq/l and for sandy dolomite, it increases from 1506±30.45 to 2924±78.96Bq/l. The activity concentrations of ^{235}U for the different samples are nearly constant with time. The reason for the higher ^{234}U concentration value is due to alpha-recoil

process, which enhances the mobilization and solubility of the decay product (^{234}U) relative to the parent (^{238}U). After the alpha-particle has been emitted, the uranium is often stabilized in solution [24, 25].Fig. (1) indicates that there is an increase in the activity towards secular equilibrium with time for ^{238}U and^{234}U.

Table (4) indicates the solubility (%) of different radionuclides for rock types measured directly after the leachates were done at time (t = 0). It is clear that, the solubility of ^{235}U is greater than that of ^{234}U, ^{238}U and ^{226}Ra. Fig (2) illustrates these solubility variations in the radionuclides for the selected rock types. It is clear that the activity of ^{238}U (%) = [(^{238}U activity concentration in leachate / ^{238}U activity concentration in rock sample) *100] for different rock types. In leachates it increases with time towards equilibrium state due to growth of ^{234}Th (Table 5). The activity (%) in siltstone & shale is very close when compared to sandy dolomite. Solubility in sandy dolomite is much less than that of siltstone & shale in spite of the high activity in the original sandy dolomite sample (Fig.3).

^{234}U/^{238}U activity ratios in the original samples were 0.85±0.15, 0.94±0.16 & 1.03±0.01 for siltstone, shale and sandy dolomite respectively.The ratios for

first measurement of the leachates were considered at t = 0 for siltstone, shale and sandy dolomite samples as 1.09±0.17, 1.4±0.21, and 1.6±0.18 respectively. The enrichment in ^{234}U is accordingly related to the crystal damage and leaching, which are the main mechanisms for the ^{234}U/^{238}U disequilibrium [12, 26].

The activity ratio of ^{238}U/^{235}U is assumed to be nearly constant (21.7).This is because that the uranium was thought to be too heavy to undergo significant isotope fractionation. The ratios between ^{238}U and ^{235}U for siltstone, shale and sandy dolomite in leachate samples are shown in Table (6) and Fig. (4). The differences in these ratios were interpreted as a result of the preferential leaching, oxidation and reduction (redox) processes .This variation is related to the increase in the activity concentration of ^{238}U with time and very little variation in ^{235}U. In case of siltstone, activity reaches almost secular equilibrium for ^{234}Th in about two half –life times. This may be attributed to the fact that the solubility of ^{235}U is more than that of ^{238}U as shown in Table (4). In addition, it is higher in siltstone & shale than that of sandy dolomite rock. It is noticed in this table that, the Ra, Th and K solubility are in low percent (5.77%, 2.22 % &1.11%) respectively. This is expected that the major remain activities will may be in the residual.

Table (1): Activity concentrations (Bq/l) ofradionuclides for siltstone leachate at different time intervals

Radionuclides	Original sample	Zero Time	After21 days	After10 days	After7 days
238U	5373±63.14	1143±22.54	1643±35.95	1832±33.34	1971±23.34
235U	245±4.69	91±1.29	96±1.66	94±1.60	98±1.32
234U	4544±785.12	1235±194.17	1891±344.98	1804±316.78	2158±197.45
226Ra	6824±18.01	394±3.41	245±3.14	294±2.88	270±2.05
214Pb	4958±6.92	5.5±0.26	45±0.92	48±0.84	46±0.65
214Bi	5011±5.62	5.4±0.22	38±0.75	41±0.72	42±0.48
232Th	50±2.36	1.1±0.11	1.3±0.12	1.7±0.13	3.4±0.22
40K	315±6.12	3.5±0.19	3.7±0.27	3.6±0.22	N.D
238U/235U	21.9±0.42	12.6±0.31	17.1±0.48	19.5±0.49	20.1±0.36
234U/238U	0.85±0.15	1.09±0.17	1.15±0.21	0.98±0.17	1.09±0.10

Table (2): Activity concentrations (Bq/l) ofradionuclides for shale leachate at different timeintervals

Radionuclides	Original sample	Zero Time	After18 days	After11 days	After6 days
238U	5843±61.64	1079±21.42	1671±29.62	1868±22.65	1921±30.39
235U	268±0.66	97±1.24	97±1.39	98±1.30	98±1.85
234U	5496±916.58	1522±227.62	1537±372.74	1788±220.23	1920±259.88
226Ra	6297±14.34	487±3.71	515±4.12	547±2.94	540±3.88
214Pb	4891±20.86	22.6±0.46	173±1.66	231±1.30	236±1.74
214Bi	4976±27.64	22.6±0.46	161±1.27	207±1.01	213±1.34
232Th	35.8±1.27	1.7±0.16	1.1±0.10	1.5±0.09	2.3±0.19
40K	213±5.11	4.2±0.20	4.4±0.26	3.8±0.18	4.1±0.26
238U/235U	21.8±0.24	11.1±0.26	17.05±0.26	19.06±0.34	19.6±0.48
234U/238U	0.94±0.16	1.4±0.21	0.92±0.22	0.96±0.12	1±0.14

Table (3): Activity concentrations (Bq/l) ofradionuclides for sandy dolomite leachate at different time intervals

Radionuclides	Original sample	Zero Time	After 18 days	After9 days	After6 days
238U	20417±167.01	1506±30.45	2047±45.00	2796±44.45	2924±78.96
235U	941±13.09	172.8±2.13	157±2.46	168±2.85	167±3.65
234U	20998±2453.70	2489±273.56	2903±489.62	2659±392.21	3544±829.55
226Ra	47299±50.53	1064±6.57	713±5.95	1217±6.85	1421±11.15
214Pb	38503±18.23	71±0.88	352±2.97	455±2.64	494±4.78
214Bi	38913±14.66	61±0.88	351±2.33	429±2.17	511±4.39
232Th	22.2±2.06	1.2±0.11	0.06±0.01	0.25±0.03	0.41±0.08
40K	112.8±11.09	1.3±0.14	N.D	N.D	6.6±0.63
238U/235U	21.7±0.35	8.7±0.21	13±0.35	16.6±0.39	17.5±0.61
234U/238U	1.03±0.01	1.6±0.18	1.4±0.24	0.95±0.14	1.2±0.29

Table (4): Solubility (%) of radionuclides for rock types measured directly after theleachates was prepared at (t = 0)

Radionuclides	Siltstone (%)	Shale (%)	Sandy dolomite (%)
238U	21.27±0.49	18.47±0.42	7.37±0.16
235U	37.14±0.88	36.19±0.05	18.36±0.34
234U	27.18±6.35	27.69±6.20	11.85±1.90
226Ra	5.77±0.05	7.73±0.06	2.25±0.01
214Pb	0.111±0.01	0.46±0.01	0.184±0.00
214Bi	0.108±0.00	0.45±0.01	0.157±0.00
232Th	2.2±0.24	4.75±0.48	5.41±0.70
40K	1.11±0.06	1.97±0.11	1.15±0.17

Table (5): ^{238}U% of different rock types at different time intervals [(^{238}U% = ^{238}U activity concentration in leachate / ^{238}U activity concentration in rock sample)*100]

Accumulated time in days	siltstone	shale	sandy dolomite
0	21.27±0.49	18.47±0.42	7.37±0.01
21	30.58±0.76	28.6±0.59	10.02±0.02
32	34.1±0.02	31.97±0.51	13.69±0.02
39	36.68±0.61	32.88±0.63	14.32±0.04

Table (6): The activity ratio (^{238}U/^{235}U) for siltstone, shale and sandy dolomite of leachates at different periods

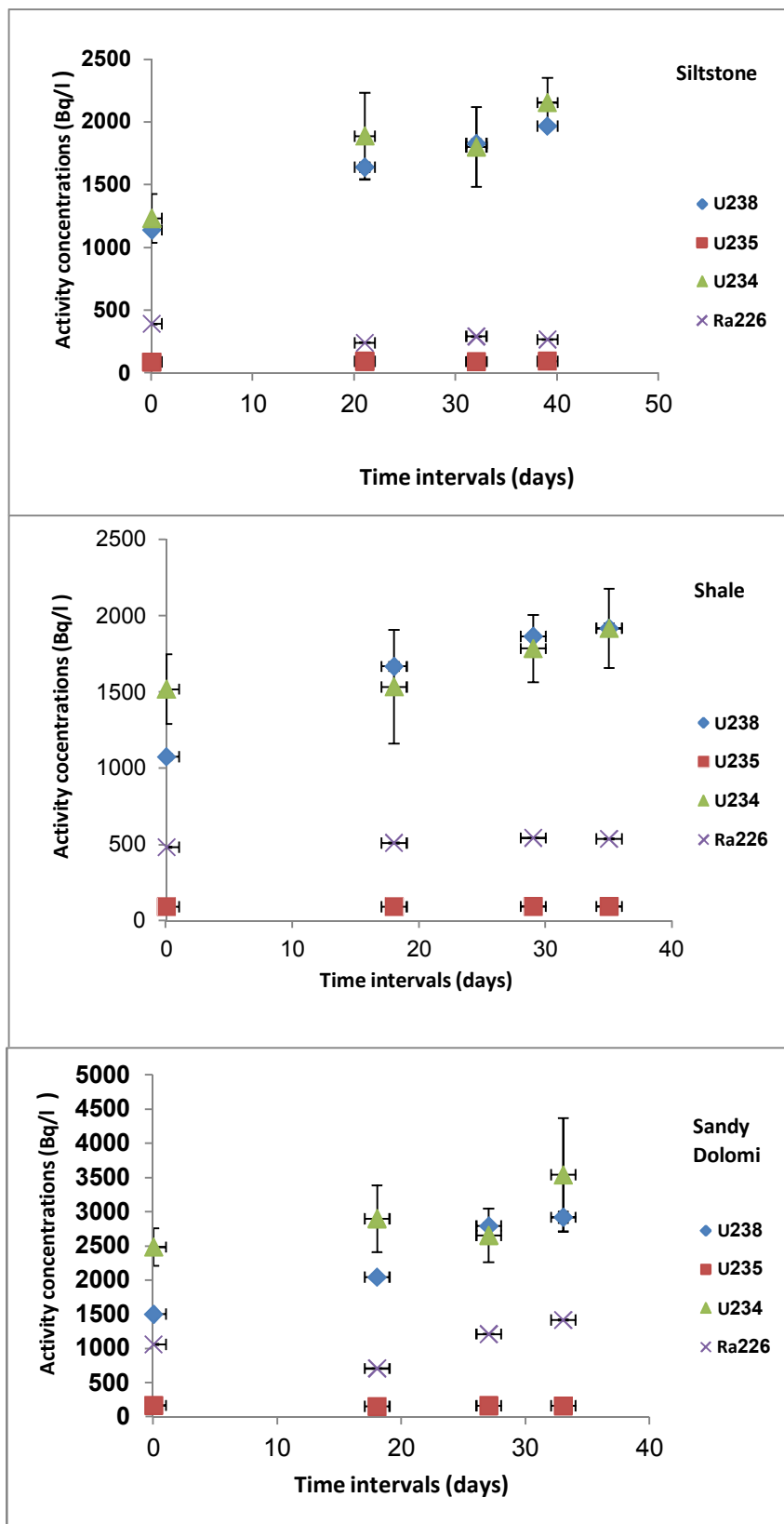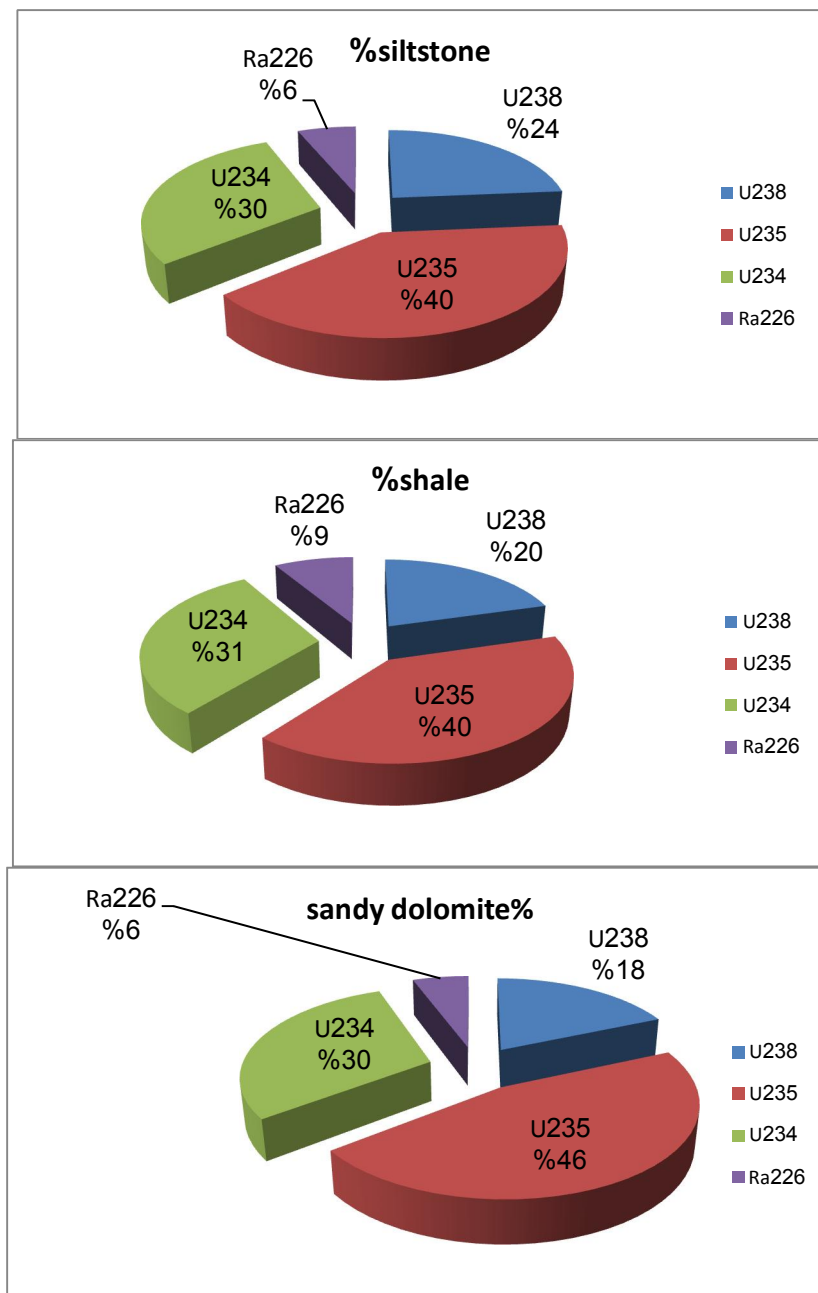| Accumulatedtime in days	^{238}U/^{235}U		
	Siltstone	Shale	Sandy dolomite
0	12.6±0.31	11.1±0.26	8.7±0.21
21	17.1±0.48	17.05±0.26	13±0.35
32	19.5±0.49	19.06±0.34	16.6±0.39
39	20.1±0.36	19.6±0.48	17.5±0.61

Fig. (1): The activity concentrations (Bq/l) for different rock samples at three timeintervals

Fig. (2): The solubility (%) for different radionuclides of different rock types starting afterleaching process was prepared.
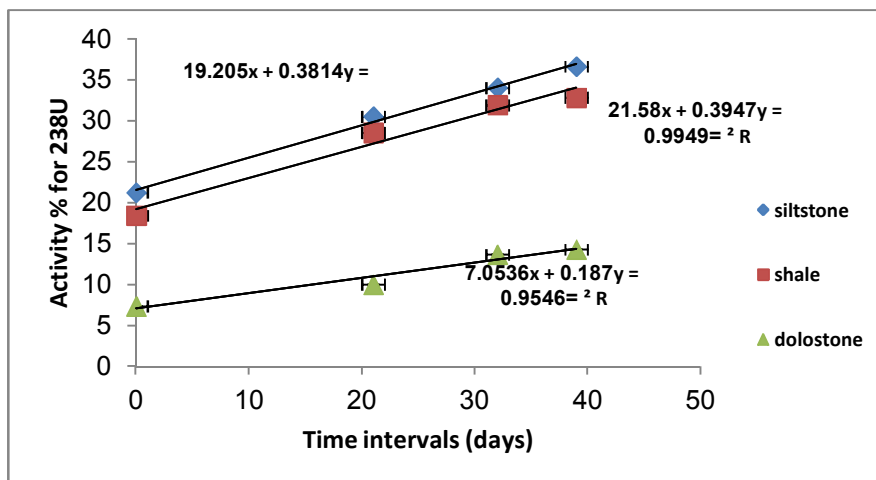
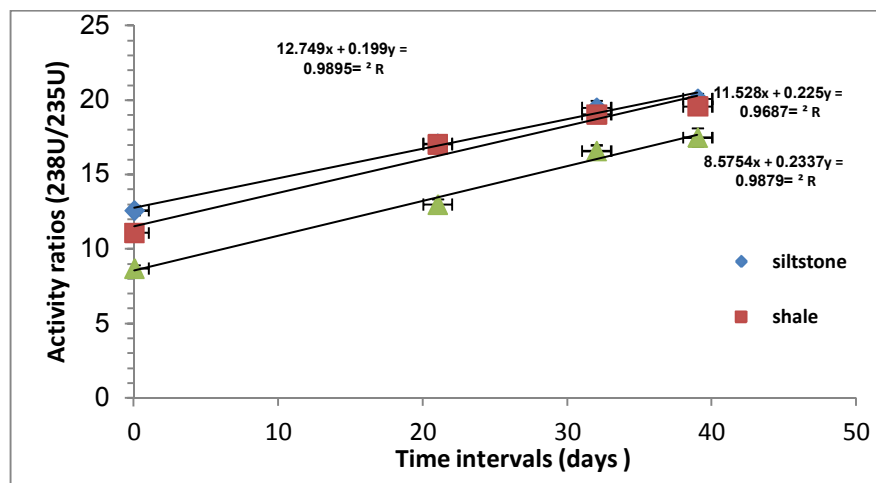**Fig. (3): Increasingofactivity (%) for ^{238}U with time for different rock types**

Fig (4): The activity ratio (^{238}U/^{235}U) for siltstone, shale and sandy dolomite at three time intervals

Conclusions

The radionuclides concentration was determined by gamma-spectrometry for three different rock samples and in their leachates at three time intervals to follow-up their distributions. The absolute efficiency calibration was performed by using threewell-known reference materials.

The activity concentrations for^{238}U and^{234}U increase towards secular equilibrium with time, while that of ^{235}U, it is nearly constant. The activity of ^{238}U (%) in siltstone & shale is very close when compared to sandy dolomite. Solubility in sandy dolomite is much less than that of siltstone & shale in spite of the high activity in the original sandy dolomite sample.

^{234}U/^{238}U ratios were obtained where most samples exhibited isotopic ratios are higher than one in leachates. This is related to the crystal damage and leaching, which are the main mechanisms for the ^{234}U/^{238}U disequilibrium. In this study, the deviation of ^{238}U/^{235}U activity ratio has been observed .This variation is related to the increase in the activity concentration of ^{238}U with time with very little variation in ^{235}U. In case of siltstone, activity reaches almost secular equilibrium for ^{234}Th in about two half –life times. Ra, Th and K solubility are in low percent. This is expected that the major remain activities are in the residual.

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