# Natural Radioactivity Level of Phosphate Fertilizers and Related Products from Al-Qaim Complex Plant in Iraq by Using Solid State Nuclear Track Detector

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**Dr. Saadi M. D. Al-Nuzal**
Environmental Research Centre, The University of technology
**Email:** saadidhaher@yahoo.com
**Dr. Sahar A. Amin**
Environmental Research Centre, The University of technology
**Muwafaq H. M. Lami**
Environmental Research Centre, The University of technology
**Basad H. Jazaa**
Environmental Research Centre, The University of technology

**Abstract**

The natural radioactivity level of phosphate rock, $P_2O_5$ (29 - 30 %), TSP, MAP, phosphoric acid, NPK, cryolite, zeolite samples obtained from Al-Qaim Complex Plant in Iraq, as well as organic bitmuse fertilizers were recorded by using solid state nuclear track detector, (SSNTD) CR-39. Three positions were selected for detectors exposure; the upper position that can record the radon originated from uranium; the middle (sample surface), and inside the sample to estimate the total alpha emitter isotopes. The measured values of the radioactivity level were found to be within the range of 113.52 - 1034.29 $Bq/m^3$ and these values belong to Cold (organic bitmuse fertilizers) and MAP-3 (Monoammonium phosphate) samples, respectively. The later was obtained from the treatment process of ~ 60 % phosphoric acid (WPA) with phosphate rock in the Wet process. Generally, the value of the total of radon and thoron radioactivity $C_a$, roughly indicated by the surface detectors, throughout the chemical process was generally twice the measurement related to uranium at the upper detector. Zeolite sample showed higher radioactivity level than phosphate rock, and this can be considered, as unexpected result for it is not famous ore for uranium scavenging.

**Keywords:** Radioactivity, Phosphate, Fertilizers, CR-39

# مستوى النشاط الإشعاعي الطبيعي للأسمدة الفوسفاتية والمنتجات ذات الصلة من مجمع معامل ألقائم في العراق باستخدام كواشف الأثر النووي للحالة الصلبة

**الخلاصة**

تم قياس مستوى النشاط الإشعاعي الطبيعي للصخور الفوسفاتية و($P_2O_5$ (29 – 30 % وTSP وMAP وحامض الفوسفوريك وNPK والكرايولايت، وعينات الزيولايت تم الحصول عليها من مدينة القائم النباتية

المعقدة في العراق، وكذلك الأسمدة العضوية bitmuse المتوفرة محلياً. تم تسجيلها باستخدام كواشف الأثر النووي الصلبة CR-39 (SSNTD). وقد تم اختيار ثلاث مواقع لوضع الكاشف في كأس القياس؛ موقع علوي الذي يسجل فيه الرادون الناتج من اليورانيوم وموقع وسطي (سطح العينة) وسفلي لتقدير مجموع النظائر الباعثة لأشعة ألفا. تبين أن القيم المقاسة لمستوى النشاط الإشعاعي نوع ألفا هي ضمن المدى 113,52 – 1034,29 بكرل/م3 وهذه القيم تنتمي إلى الأسمدة العضوية نوع كولد (Cold) وMAP-3 نموذج أحادي فوسفات الامونيوم، على التوالي. أما القياس الأخير فكان لناتج عملية المعالجة الرطبة (WPA) للصخور الفوسفاتية بحامض الفوسفوريك. كانت قيمة النشاط الإشعاعي الكلي للرادون والثورون $C_a$، التي سجلها الكاشف على السطح، في جميع مراحل العملية الكيميائية بشكل عام ضعف تلك المسجلة لليورانيوم. وأظهرت عينة الزيولايت أعلى مستوى للنشاط الإشعاعي من صخور الفوسفات، وهذا يمكن اعتبارها نتيجة غير متوقعة، لأنه خام غير مشتهر باحتجازه لليورانيوم.

**الكلمات المرشدة:** نشاط اشعاعي، مخصبات، فوسفات، كاشف الأثر، CR-39.

## INTRODUCTION

Measuring the radioactivity level in different soils [1-4], building materials [5-6], environment [7-8], ores, and phosphate fertilizers was performed by many workers. Phosphate rocks contains significant amount of radioactive materials, and uranium concentration in different phosphate ores from different places around the world range from 5.17 ppm up to 221 ppm [9]. Their presence can be related to the nature of phosphates ability to bound and retain them as compounds, complexes or both scheme, as well as the limited solubility of these phosphates.

Iraq is one of the leading countries in phosphate industry, and its estimated phosphate rock deposits at four sites in the Western desert (Akashat, Ethna, H3, and Swab) to be more than 5,750 Mt, which would be 9 % of the world's total phosphate rock reserves. Al-Qaim Complex Plant main task is to raise the quality of the phosphate rock introduced from Akashat from 21 % $P_2O_5$ to 30 % $P_2O_5$ in order to be appropriate for phosphoric acid and phosphate fertilizers industry. Many unites in this plant can produces phosphoric Acid, Triple Sodium Phosphate ($Na_3PO_4$, TSP), Monoammonium phosphate ($NH_4H_2PO_4$, MAP), compound fertilizer (NP, NPK), cryolite ($NaAlF_6$), and Zeolite [10-11].

Phosphate deposits contain the naturally occurring radionuclides $^{238}U$ and $^{232}Th$ together with their decay progeny, among them fourteen alpha and eleven beta emitting nuclides. Rock phosphate deposits contain many million tons of uranium, which may be extracted as a by-product of making fertilizers. Some 20,000 tons of uranium has already been obtained from these rock phosphate deposits, but the process became uneconomic in the 1990s. During the chemical treatment of the phosphate rock, the U and Th equilibria are disrupted and the radionuclide's migrate to intermediate, final products, by-products and waste, according to their solubility and chemical properties [12-14].

Although different type of rocks such as phosphate, phosphogypsum rocks are a major source for phosphate in fertilizers, they represent very low radiation hazards,

potential radiological impacts resulting from direct exposure, inhalation and ingestion of foods grown with fertilizers are expected [15-19].

Exposure to radon originating from phosphate industry is one of the main health concerns associated with the use and disposal of this material **[20]**. Radon exhalation from phosphogypsum may pose a health risk to workers on a stack or people living in houses equipped with phosphogypsum panels or build on an area which used to be agricultural land treated with phosphogypsum as soil amendment [8-9].

This work describes a simple method to measure exhalation rate of $^{222}Rn$ from phosphate rocks and phosphate and bitmuse fertilizers in a laboratory and in economical procedure with help of solid state nuclear track detectors, (SSNTD) CR-39 to assess the excessive radiological impact due to increased radon exhalation.

**Materials and methods**

Phosphate rock, $P_2O_5$ (29 - 30 %), TSP (2), MAP (3), phosphoric acid, NPK, cryolite, zeolite were supplied by State Company for Phosphate. Organic fertilizers Al-Fiafi, Natural ado, and Cold were purchased from local dealers. Samples were crushed by jaw crusher to a size of about 5 mm thick granules, and then further processed in ball mill for 20 min fine grinding. The last operation was repeated until all the powder passed through 75 μm mesh sieve.

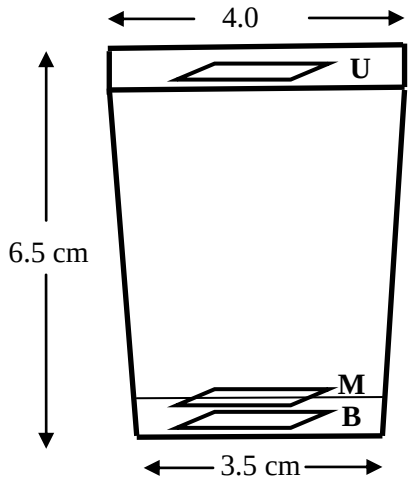


**Figure (1). The CR-39 SSNTDs detector used in this study, which is a plastic container (top and bottom radius of 2.0 cm and 1.75 cm respectively).Identical shaped CR-39 SSNTDs, 250 μm, 1.5 cm × 1.0 cm have been separately placed in three positions for the CR-39 SSNTDs relative to the sample were selected (U, M, and B).**

Radon exhalation rate was measured by closing the sample in a plastic container (top and bottom radius of 2.0 cm and 1.75 cm respectively, Figure-1), samples of 10.00 g, and were placed in it. Identical shaped (SSNTD)s CR-39, 250 μm, 1.5 cm ×

1.0 cm have been separately placed at a distance 6.0 cm above the sample for 90 days. Three positions for the CR-39 SSNTDs relative to the sample were selected. The upper position (U) was meant to record the radon originated from Uranium; the middle (M) in which the detector was placed on sample surface, and the bottom (B) in which the detector was placed on inside the sample to have an estimate for the total radon originated from uranium, thorium, and any other alpha emitter. The longtime of irradiation (90 days) is necessary to accumulate considerable number of tracks of α-particles that emitted from radon. After the irradiation, the exposed films were developed in NaOH solution for chemical etching conditions 6.25 N at $70^0$C for 7 hours for CR-39 films. After the chemical treatment, the visual counting of alpha particles tracks are carried out by means of an optical microscope 40X.

**Theoretical consideration**

Theoretical calculations of the calibration factor (K) was performed by adapting the model presented by Barillon *et al.* [21], as well as that of Sarma for expressing the alpha radioactivity in term of radium concentration ($Bq.kg^{-1}$) [1]. The calibration factor K [$(track/cm^2)/(Bq.m^3.day)$ or the response of CR-39 nuclear track detectors depend on many parameters, among them is the fraction of alpha emitters present in air, cup wall dimension, the type of used detector via etching conditions **[11-12]**.The integrated Radon concentration can be calculated from the Track density ρ($tracks.cm^{-2}$) is related to the radon activity concentration $C_a$ ($Bq.cm^{-3}$) and the exposure time T (days) from the formula [1, 21]:

$$\rho = KC_aT \quad \text{or} \quad C_a = \rho/KT \qquad (1)$$

Where ρ is the track density ($Tr\backslash cm^2$), K is the diffusion constant, $C_a$ is the Rn concentration in air space of the cup expressed in ($Bq\backslash cm^3$), and T is the radiation time h.

Diffusion constant (K) for the solid samples can be determined from the following relation due to the dimensions of the technique [21]:

$$K = (1/4)r[2\cos\theta_t - r\backslash R_\alpha] \qquad (2)$$

Where r is the cup average radius for the diffusion volume, $\theta_t$ is the threshold angle for the CR-39detector ($35^o$), $R_\alpha$ is the range of alpha particle in air which is 4.15cm.

The Radon concentration in the samples can be calculated from the following relation [1, 21]:

$$C_s = C_a\lambda_{Rn}Ht/L \qquad (3)$$

Where $C_s$ is Rn concentration in the samples expressed in ($Bq\backslash m^3$), $C_a$ is the Rn concentration in air space ($Bq\backslash m^3$), $\lambda_{Rn}$ is the decay constant for Rn, H is the height of air space in the cup, L is the thickness of the sample, and t is the irradiation time.

The activity of radon $A_{Rn}$ in Bq exhaled from the sample from the relation:

$$A_{Rn} = C_s V \quad (4)$$

$$\text{Where: } V = \pi r^2 L \quad (5)$$

**Results and discussion**

The final and related downstream products radioactivity level of Al-Qaim Complex for Phosphates Fertilizers were measured by using CR-39 SSNTDs technique. Among these are phosphate rock, $P_2O_5$ (29 - 30 %), samples of TSP, MAP, phosphoric acid, NPK, cryolite, zeolite studied, as well as three organic fertilizers (Al-Fiafi, Natural ado, and Cold from local Iraqi dealers)for comparison. Synthetic fertilizers are made by chemically processing raw materials. Figure-2 showed the general process followed in this plant to convert phosphate rocks to $P_2O_5$ (29 - 30 %), in beneficiation process prior to the wet process to convert it to phosphoric acid, and then to TSP, MAP, NPK fertilizers in separate units. The process include three different chemical treatments with three locally produced chemicals, which are sulfuric acid, nitric acid, and ammonia. The process for manufacturing MAP is relatively simple. In a common method, a one to one ratio of ammonia ($NH_3$) and phosphoric acid ($H_3PO_4$) is reacted and the resulting slurry of MAP is solidified in a granulator [16]. Organic fertilizers are made from naturally occurring mineral deposits and organic material, such as bone or plant meal or composted manure.

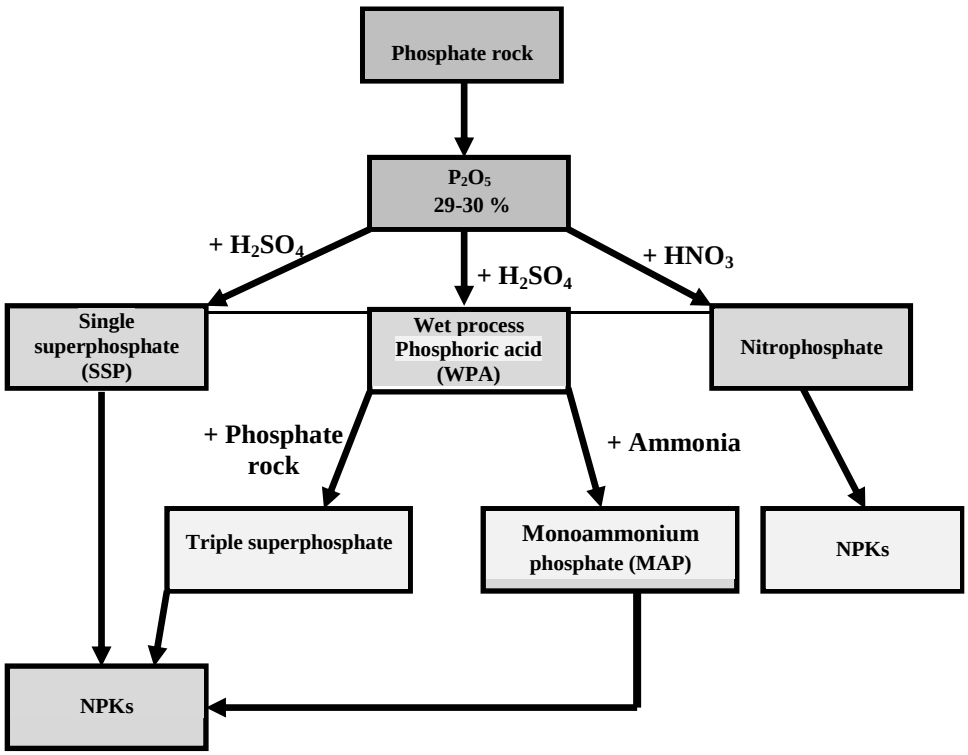


**Figure (2). The general production process used by Al-Qaim Complex to convert phosphate rock, $P_2O_5$ (29 - 30 %), TSP, MAP, Phosphoric acid, and NPK (van**

**Kauwenbergh S.J. (2002). Cadmium content of phosphate rocks and fertilizers.** ***International Fertilizer Industry Association (IFA) Technical Conference*****, p. 31.September 24-27, Chennai, India)**

The radioactivity level measurements, $C_a$ (Bq/$m^3$) of all samples, were presented in Table-1, and illustrated in Figure 3 for the purpose of comparison and discussion. Hence three positions were used for the measurements, viz. upper, middle and bottom positions, the results showed that the radioactivity level of the upper position detectors read the lowest values. It is apparent that the top detector can read the radioactivity of the exhaled alpha emitting radon $^{222}_{88}$Rn gas, with a half-life of 3.82 day, originated from the decay uranium chain, for all samples, as shown in Figure-3. This gas has a good chance to reach the top detector and can be recorded as the activity of the samples in term of radon, uranium or radium. Other radioisotopes, particularly the alpha emitting thoron $^{220}_{88}$Rn has no chance to reach the top detector, for its very short half-life of 56.6 seconds and hence the top detector reading is limited only for radon $^{222}_{88}$Rn. The recorded radioactivity on the middle detector is relatively higher than that on the top by at least two fold, this is not a surprise because thoron gas (another radon isotope $^{220}_{88}$Rn with short halve life of 55.6 second) has a reasonable chance to reach the sample surface. There is a good possibility for the other radioactive alpha emitting isotopes at the surface of the sample to increase the recorded radioactivity level. These isotopes originate from the decay schemes of uranium and thorium, viz. $^{238}_{92}$U, $^{234}_{92}$U, $^{232}_{90}$Th, $^{230}_{90}$Th, $^{228}_{90}$Th, $^{226}_{88}$Ra, $^{224}_{88}$Ra, $^{222}_{86}$Rn, and $^{220}_{86}$Rn, as shown in Figure-5. The bottom detectors showed even much more radioactivity than that of the middle detector that sometimes is twenty fold higher. This is the general case for all the samples, in which the order of radioactivity level reading for the three position of the detectors is in the following sequence: bottom detector > middle detector > top detector.

**Table (1). The recorded values of of the radioactivity level of track/cm$^2$, $C_a$, $C_s$, and $C_U$ (ppm)**

| # | Sample | Top detector | | | Surface detector | | Bottom detector | |
|---|---|---|---|---|---|---|---|---|
| | | Track No./cm$^2$ | $C_a$ (kBq/m$^3$) | $C_s$ (kBq/m$^3$) | Track No./cm$^2$ | $C_a$ (kBq/m$^3$) | Track No./cm$^2$ | $C_a$ (kBq/m$^3$) |
| 1 | Phosphate rock | 4256.165 | 984.14 | 192.81 | 9347.653 | 2161.45 | 85839.299 | 19848.33 |
| 2 | $P_2O_5$ 29-30 % | 8074.781 | 1867.10 | 365.79 | 70047.732 | 16196.90 | 98886.237 | 22865.13 |
| 3 | Phosphoric acid | 5051.710 | 649.65 | 127.27 | 11296.738 | 2612.11 | 13683.373 | 3163.96 |
| 4 | TSP-1 | 3699.284 | 2057.42 | 403.07 | 19649.960 | 4543.59 | 20922.832 | 4837.91 |
| 5 | TSP-2 | 5608.591 | 1296.86 | 254.07 | 12569.610 | 2906.43 | 15035.799 | 3476.68 |
| 6 | MAP-1 | 17859.984 | 4129.70 | 809.06 | 36793.953 | 8507.74 | 38106.603 | 8811.26 |
| 7 | MAP-2 | 12211.614 | 2823.65 | 553.19 | 44749.403 | 10347.25 | 48050.914 | 11110.65 |
| 8 | MAP-3 | 22832.140 | 5279.40 | 1034.29 | 53420.843 | 12352.32 | 64240.254 | 14854.05 |
| 9 | NPK | 5171.042 | 1195.68 | 234.25 | 12092.283 | 2796.10 | 39777.247 | 9197.56 |
| 10 | Cryolite | 6125.696 | 1416.42 | 277.49 | 6483.691 | 1499.20 | 10580.747 | 2446.55 |
| 11 | Zeolite | 7159.904 | 1655.56 | 324.34 | 88066.825 | 20363.39 | 124303.898 | 28742.36 |
| 12 | Al-Fiafi | 7557.677 | 1747.546 | 342.37 | 8273.667 | 1913.09 | 44558.472 | 10303.10 |
| 13 | Natural ado | 4256.165 | 984.14 | 192.80 | 4733.492 | 1094.51 | 17024.661 | 3936.55 |
| 14 | Cold | 2505.966 | 579.45 | 113.52 | 6006.364 | 1388.83 | 9307.875 | 2152.23 |

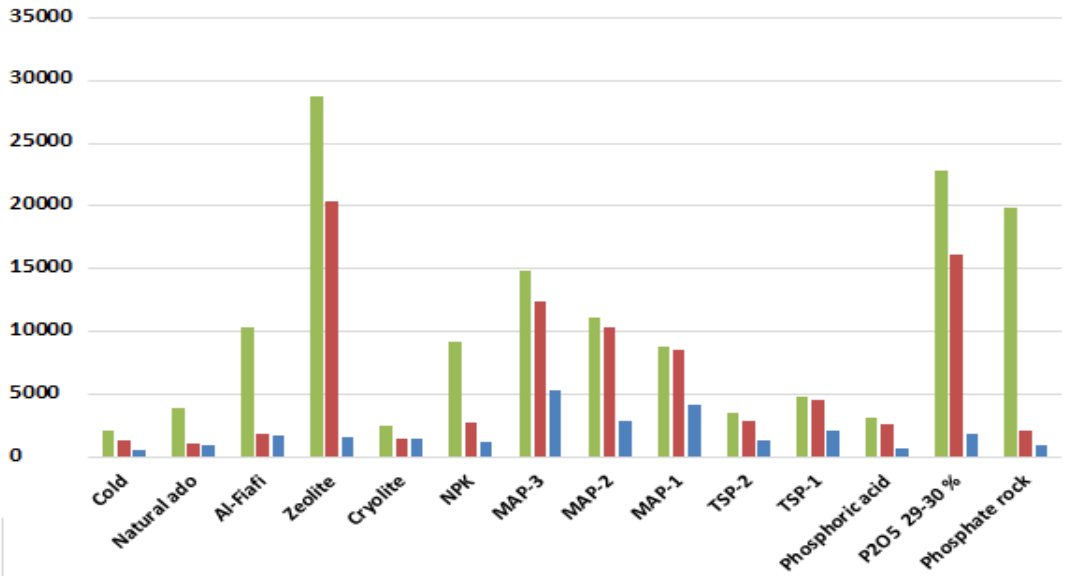


**Figure (3). The recorded values of the radioactivity level, $C_a$ (kBq/m$^3$)**

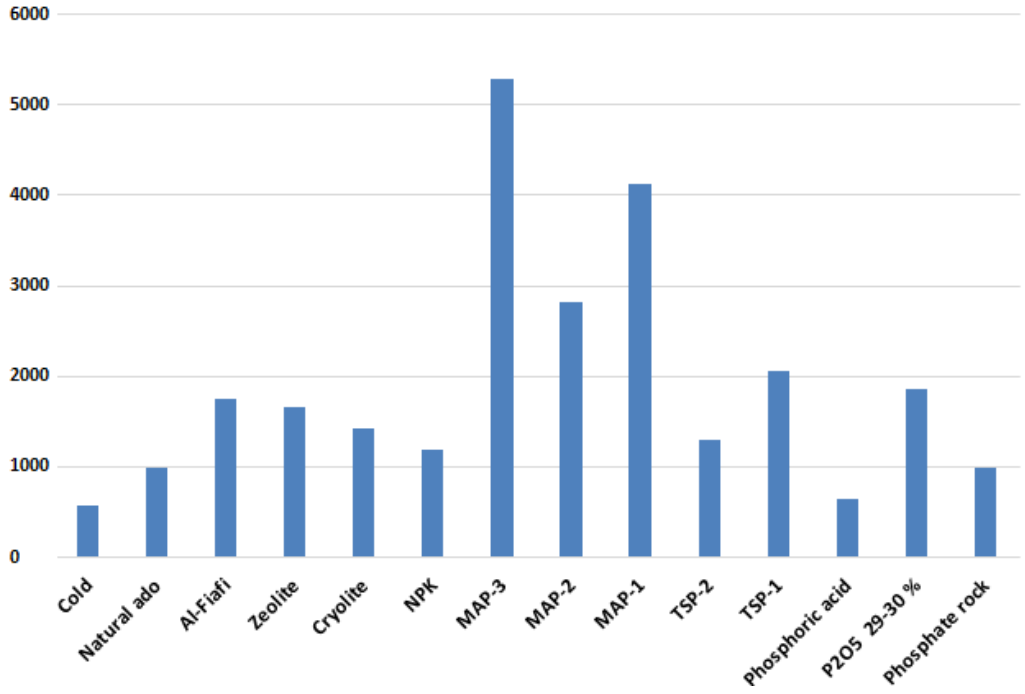


**Figure (4). The calculated values of the radioactivity level $C_s$ (kBq/m$^3$)**

Surprisingly the highest level of the radioactivity was recorded for zeolite sample by the bottom and middle detectors has the level of 28742.36 and 20363.39 Bq/m$^3$, respectively. This is an unexpected result because the typical process followed to produce this product entail heating aqueous solutions of alumina and silica with sodium hydroxide. The only possible source of

radioactivity will come from alumina minerals. The lowest level of the radioactivity was recorded by the bottom, middle, and top detectors of the organic bitmuse (Cold), with a value of 21522.23, 1388.83, and 579.45 Bq/m$^3$, respectively. The obtained value is supposed to be reasonable because there is no considerable source of uranium or thorium.

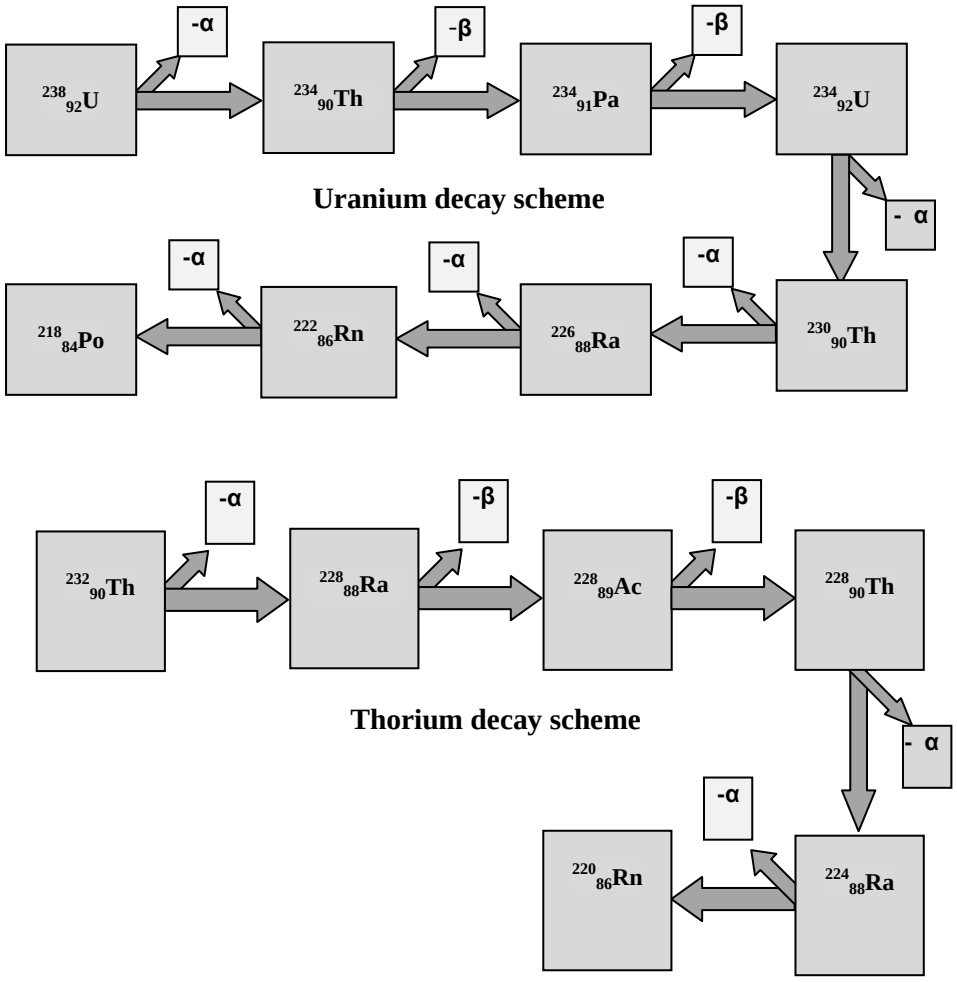


**Figure (5). The decay schemes of uranium $^{238}_{92}$U, which give the daughter nuclide as a radioactive radon gas $^{222}_{88}$Rn, and thorium, which gives the very short-lived thoron $^{220}_{86}$Rn**

The level of the radioactivity in phosphate rock indicate the presence of uranium and higher level of thorium. In this case, one can consider the middle detector as indicator, which is a bit higher than the total radon and thoron. In other word, the reading of the middle detector will be the sum of $^{220}_{88}$Rn and $^{222}_{88}$Rn as well as some other alpha emitting species from the sample surface. Figure-5 showed the decay

scheme of uranium, which include the following alpha emitting nuclides $^{238}_{92}U$, $^{234}_{90}Th$, $^{234}_{92}U$, $^{226}_{88}Ra$, $^{222}_{86}Rn$ and that of thorium decay scheme, which include $^{232}_{92}Th$ and $^{228}_{88}Ra$. The results showed that the concentration of uranium correlates with the $P_2O_5$ concentration in the type of fertilizers and that the $^{232}Th$ series contributes only in a minor way to the radioactivity in phosphates compared to the uranium series. The downstream process of fertilizers include the treatment of phosphoric acid with alkali, e.g. sodium hydroxide, ammonia, or phosphate rock.

## Conclusion

Generally, the value of thoron radioactivity, $C_a$, indicated by the surface detectors, throughout the chemical process was generally twice that related to uranium. The measured values of the radioactivity level was found to be within the range of 113.52 - 1034.29 Bq/m$^3$, and these values belong to Cold (organic bitmuse fertilizers) and MAP-3 (Monoammonium phosphate) samples, respectively. Unusually, Zeolite sample showed higher radioactivity level.

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