Chapter 4

Environmental Radioactivity of TE-NORM Waste Produced from Petroleum Industry in Egypt: Review on Characterization and Treatment

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1. Introduction

At present time the different environmental compartments suffer from excessive accumulation of various toxic pollutants, hazardous fallout contaminants and several naturally occurring radionuclides, including potassium-40, thorium and uranium with the natural decay series of Th and U as well as several other man-made radionuclides. It is now of common practice to regulate any uncontrolled release of hazardous wastes in different environmental compartment [1]. Toxic hazardous wastes are defined as containing chemicals posing substantial hazards to human health or to the environment when improperly treated, stored, transported, or disposed. Scientific studies show that these wastes have toxic, carcinogenic, mutagenic, or teratogenic effects on human or other life forms. The majority of hazardous waste is generated by the chemical manufacturing, petroleum, pesticides and coal processing industries. Hazardous wastes may enter the body through ingestion, inhalation, absorption, or puncture wounds [2].

Naturally Occurring Radioactive Materials (NORM's) are those materials that contain radioactive elements what are found naturally in the earth's environment. Examples of these radioactive elements are the ^{238}U, ^{235}U, ^{232}Th series and their respective decay daughter, as well as ^{40}K. NORM's exist in soil, water, plants, animals, human, coal, lignite, petroleum, phosphate ores, geothermal wastes, wastewater…etc., in small but varying amounts almost everywhere [3].

On the other hand, nearly all the naturally occurring radioactive materials are considered in balance state. However, in several industrial processes e.g., mining of minerals (U, Th, steel, rare earth's metals), phosphate, oil and gas production, concentration of the natural radionuclides may be altered than its physical state, and exists in concentrations over than that exists naturally.

Wastes associated with the various industrial activities, with enhanced levels of the natural radioactivity as a result of industrial process, causes what is called, "Technological Enhanced-Naturally Occurring Radioactive Materials", to be named as acronym word "**TE-NORM**". For instance, TE-NORM scales may build up inside of oil field production tubing and may concentrate considerable quantities of radioactive material that has the potential to expose humans to relatively high dose of radioactivity. TE-NORM is often precipitated as sludge and scales. The human body cannot sense or detect TE-NORM, so, it can be detected and measured indirectly through their ionizing radiation using specialized instrumentation [4]. Uncontrolled release of activities associated with enhanced levels of NORM can contaminate the environment and pose a risk to human health. These risks can be alleviated by the adoption of controls to identify where NORM is present; and by the control of NORM-contaminated equipment and waste while protecting workers.

1.1. Discovery TE-NORM in industry

The history of TE-NORM in oil and gas production follows closely in history of the discovery of radioactivity in the first part of 20th century. We must remember that, the discovery of radioactivity is more than one hundred years old. In 1918, a Canadian paper was published on radioactivity in natural gases. In the 1930's an elevated radium level were detected in the Russian oilfields. In 1953, the US geological society published a paper on uranium and helium in gas formations. In 1973, (EPA) performed a study on the presence Rn-222 natural gases [5-8].

A number of major oil companies helped sponsor a study on radon in natural gas products that was completed in 1975. The thrust of this study was the potential effect that radon would have on the consumer of natural gas products. Radon contamination of natural gas has been known for nearly 100 years [9]. These studies concluded that, radon in natural gas products does not present any hazard to the consumer. However, that radon could be a problem for different processing industries and some research efforts have focused on this concern [9-10].

In 1981, scale produced on offshore oil platforms in the North Sea was found to contain TE-NORM in significant quantities. These findings were presented in a 1985 offshore technology conference paper on radioactive scale formation in Houston, Texas, USA. Consequently, industry and government officials were aware of the possibility that TE-NORM scale could be present in US domestic operations. In 1986, significant TE-NORM scale was found in Laurel, Mississippi (USA). Some rather alarming press headlines and featured articles followed shortly in both Mississippi and Louisiana after the presence of TE-NORM in the oil path became better known. These articles stressed the fact that there are no current regulations, either by USA or other federal governments controlling this radioactive waste and called for their creation and enforcement. Since TE-NORM was first re-discovered domestically, the oil and gas industry has responded progressively to TE-NORM issues by notifying appropriate state agencies, initiating field surveys and studies to characterize and locate occurrence of TE-NORM in conjunction with the American Petroleum Institute,

informing other oil and gas operations, employees and contractors, and reviewing operating practices [5].

TE-NORM contamination of oil and gas industry petroleum equipment has been identified world- wide, e.g. USA (Alaska, Gulf of Mexico region), the North Sea region, Canada, Australia, several Middle East countries (Egypt, Saudi Arabia...etc.). Since 1918 till 1980, most researches were focused on the TE-NORM contamination of natural gas facilities, and the contamination is attributed to ^{226}Ra as well as ^{222}Rn gas and its decay products, e.g. ^{218}Po, ^{214}Pb, ^{214}Bi, and ^{210}Pb. Within the text, the activity concentration ranges from background level to several hundreds Bq/g (^{226}Ra). Doses to workers involved in handling, contaminated equipment, or waste are usually very low, and the main problem related to radioactive deposits is waste disposal [11]. The presence of TE-NORM or naturally occurring radionuclides in the product materials from oil and gas facilities, give rise to deposits with enhanced levels of these radionuclides in the processing equipment [12].

1.2. Origin and formation of TE-NORM

In nature, there are three naturally occurring radioactive decay series. The first series, known as thorium series, consists of a group of radionuclides related through decay in which all the mass numbers are evenly divisible by the number four, (4n) series. This series has its origin radionuclides Th-232, its abundance is 100%, specific activity is 2.4×10^5 dpm/g, which undergoes α -decay with a half-life of 1.41×10^{10} y. The terminal nuclide in this decay series is the stable Pb-208. In this series, the transformation from the original parent Th-232 to the finial product Pb-208 requires 7α and 4β -decays. The long-lived intermediate is 6.7 y for Ra-228, Fig. (1).

The second series is the uranium series, which consists of group radionuclides that, the parent radionuclide in this series is U-238 (4n+2) abundance = 99.27 %, which undergoes α -decay with a half-life of 4.47×10^9 y. The stable product of the uranium series is Pb-206, which is reached after 8α and 6β -decay steps, Fig. (2). This is a particularly important series in nature since it provides the more important isotopes of elements Ra, Rn and Po, which can be isolated in large amounts in the processing of uranium minerals. Each ton of uranium is associated with 0.34 g of Ra-226.

The third radioactive decay series, (4n+3) known as the actinium series, the head of this series is U-235, which has an abundance of 0.72 % and a half-life of 7.1×10^8 y for α -decay. The stable end product of this series is Pb-207, which is formed after 7α and 4β -decay steps. The specific activity of U-235 is 4.8×10^6 dpm/g, Fig. (3) [13].

Other important radionuclide that exists in the nature is potasium-40 ($t_{1/2.}$ 1.28×10^9 y, isotopic abundance 0.0118 %). K-40 is found in plants, animals and in human bones. It is widely distributed in nature with volume concentrations ranging from 0.1 to 3.5 % in carbonates (limestones). The bones of an average human body contain concentrations of ~ 17 mg of K-40. The average radiation dose received from K-40 is 0.25 mSv/y to tissue and ~ 0.36 mSv/y to bone.

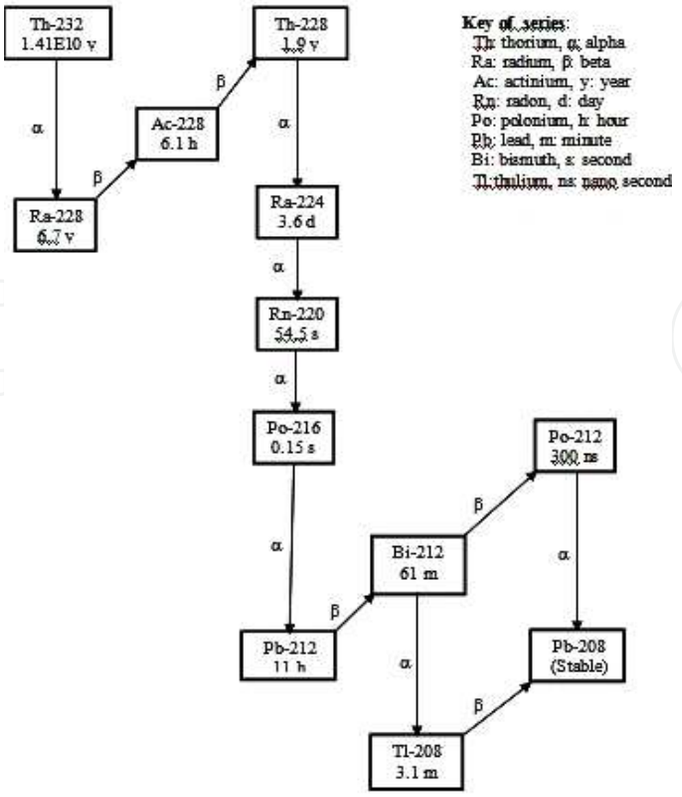

Figure 1. Scheme of the thorium decay (Th-232) series.

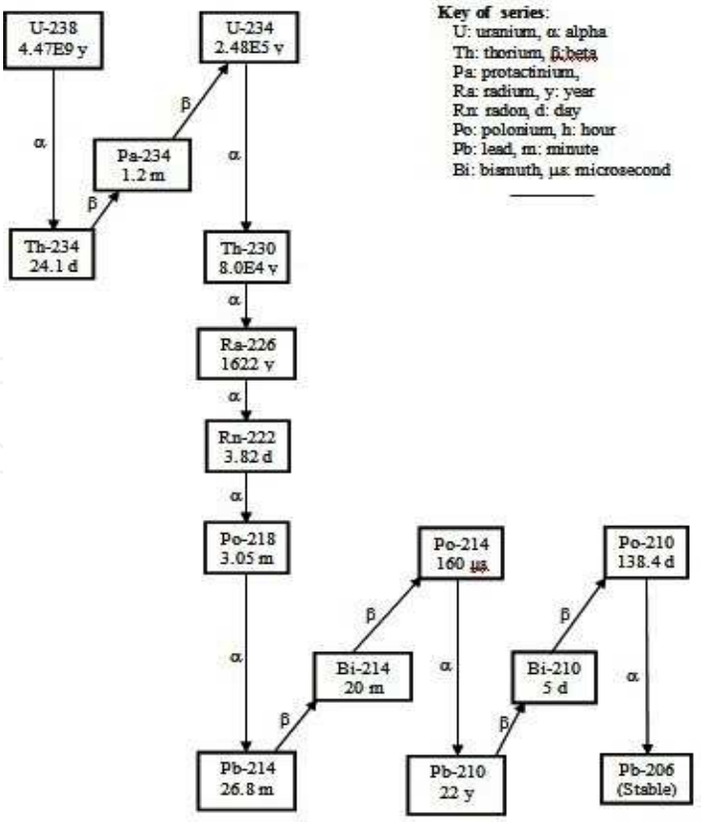

Figure 2. Scheme of uranium (U-238) decay series.

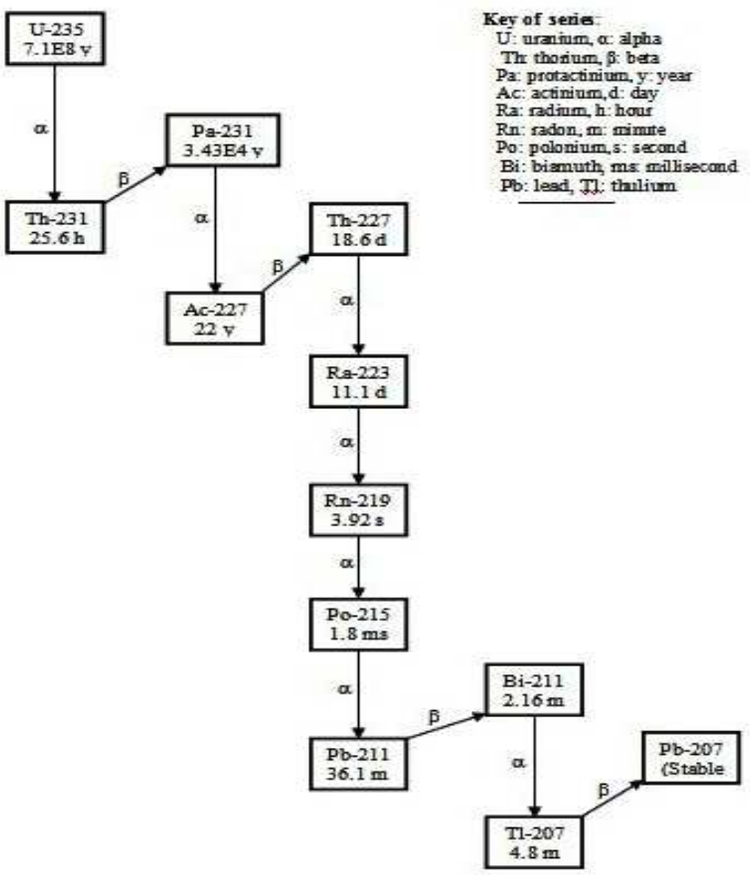

Figure 3. Scheme of actinium (U-235) decay series.

Radioactive materials such as uranium and thorium were incorporated in the Earth's crust when it was formed; these normally exist at low concentrations in rock formations. Decay of these unstable radioactive elements produces other radionuclides that, under certain conditions (dependent upon pressure, temperature, acidity *etc*) in the subsurface environment are mobile and can be transported from the reservoir to the surface with the oil and gas products being recovered. During the production process, NORM flows with the oil, gas and water mixture and accumulates in scale, sludge and scrap materials. It can also form a thin film on the interior surfaces of gas processing equipment and vessels. The level of NORM accumulation can vary substantially from one facility to another depending on geological formation, operational and other factors. To determine whether or not a facility has NORM contamination, NORM survey, sampling and analysis needs to be conducted. Table (1) gives the physical information for selected natural occurring radionuclides.

The TE-NORM waste occurs though the extraction and treatment of liquid and gases hydrocarbons and is generally accompanied by the formation and accumulation of radioactive scales, sludges and films. The petroleum waste (scale or sludge) was produced by two mechanisms either incorporate or precipitate into the production equipment such as pipelines, tank storage, pumps etc. The TE-NORM waste as scale and sludge generated in oil and gas equipments is due to the precipitation of alkaline earth metals as sulphates, carbonates, and/or silicates [9].

Nuclide	Half-life	Decay mode (energy)+	Γ * (R/hr)/Ci	Formation method	Uses
^{40}K	1.28×10^{9} y	β-(1.31 MeV) γ (1.46 MeV)	0.0817	Primordial NORM	Geologic dating
^{222}Rn	3.8 days	α (5.49 MeV) γ (512 KeV)	2.73×10^{-4}	^{238}U decay series	Patient medicines
^{226}Ra	1600 yrs	α (4.78 MeV) γ (186 KeV)	0.0121	^{238}U decay series	Luminous products
^{232}Th	1.4×10^{10} yrs	α (4.01 MeV) γ (12 KeV)	0.0684	Primordial NORM	gas lantern mantles
^{235}U	7.04×10^{8} yrs	α (4.40 MeV) γ (186 KeV)	0.339	Primordial NORM	Nuclear reactor fuel,
^{238}U	4.47×10^{9} yrs	α (4.20 MeV) γ (13 KeV)	0.0652	Primordial NORM	Military uses (armor, shells)
^{208}Tl	3.05 min	β (1.79 MeV) γ (2.6 MeV)	1.70	^{232}Th decay series	none

+ beta energies given are maximum decay energy, alpha and gamma energies are for the most probable decay energy

* given gamma constant reflects radiation dose in air as distance of one meter. The gamma constant (Γ) can be used to determine radiation dose from a gamma emitting radionuclide. The higher the value of gamma constant, the higher radiation dose. So, for example, the radiation dose from ^{235}U will be higher than the radiation dose from ^{238}U.

Table 1. Physical information for selected naturally occurring Radionuclides [14]

Some investigations were performed concerning the composition and characterization of the formed radioactive TE-NORM waste produced during oil and gas processing. Nuclear spectroscopic analysis showed that, the main radionuclides present in these wastes are traces of ^{238}U and ^{232}Th as well as their decay daughters. These studies indicated that the incorporation and co-precipitation of these natural radionuclides with alkaline earth metals (e.g., Mg, Ca, Sr, Ba) and some quantities of lead as sulphates, carbonates and/or silicates [15]. Some other studies were also performed under controlled production conditions, proved that, the factors that are greatly responsible for the formation of radioactive scale and/or sludge are water composition. The way in which the scales are deposited is connected to the pipes, superficial features, fluid-dynamic phenomena and crystallization kinetics. Testa et al. found that, variations in sulphates and carbonate solubility can give rise to scale formation, which are connected to some physical and chemical factors, e.g., temperature variation, pressure changes, pH-balance, evaporation in the gas extraction pipes and injection of incompatible sea waters. Also, the re-injected water into the reservoirs to maintain the production pressure during the field exploration seemed to be a principal cause for the scale formation [16]. As a consequence of the physical and chemical processes during the extraction of oil, besides the production water additional scale is obtained. Scale production in gas and oil field equipment is due to precipitation of alkaline earth metal sulphates or carbonates according to the following chemical reactions:

$$Ca^{+2} + CO_3^{-2} \rightarrow CaCO_3$$

$$Sr^{+2} + SO_4^{-2} \rightarrow SrSO_4$$

$$Ba^{+2} + SO_4^{-2} \rightarrow BaSO_4$$

Therefore, the observed levels of activity concentrations both in the separated sludge and solid scale are much higher than those observed in the produced water from the oil industry. Many of the physical characteristics of oil formations, high temperature pressure,..etc. tends to increase the radionuclide solubility in production fluids. This due to the complex process for sludge formation. Generally, uranium and thorium are relatively insoluble and remain stationary in the reservoir, while, radium is more soluble and may become mobilized in the produced water phase of the reservoir. It has been estimated that: 25000 tones of TE-NORM contaminated scale, and 225000 tones of TE-NORM contaminated sludge, are generated each year by the petroleum industry. The available data indicate that, the total radium levels to extreme measurements of 15.17 kBq/g scale and 25.9 kBq/g in sludge [17].

Many industries produce wastes that might contain natural radionuclides. Some of industries producing TE-NORM are coal, petroleum and natural gas, tungsten, phosphate fertilizer production, mineral processing, zirconium minerals or sand, welding and ceramics and building materials industry. In this review, we are interested in petroleum and phosphate industries that are the important industries in Egypt.

1.3. Characterization and radiological assessment

Some analytical and radiometric techniques are used to identify the chemical composition and radioactivity level of samples. The main phase composition of samples has been carried out using a powder X -ray diffractormeter equipped with a copper target and a nickel filter. The micro and trace-elemental analysis of samples have been performed by X -ray fluorescence (XRF) spectrometer. The IR spectra of the samples under study were done using FT-IR spectrometer. The different naturally occurring radionuclides present in the tested samples, were identified and the concentration of their radioactivity levels were detected and determined using a typical non-destructive nuclear spectroscopic technique. This has been performed using γ -ray spectrometer equipped with a High Purity Germanium (HPGe) detector.

The test sample containing different radionuclides was measured by γ -ray spectrometry, the specific activity (Bq/kg) of this unknown sample will be calculated using the following equation [18,19]:

$$A = \frac{C_{i,e}}{\varepsilon_{i,e} \times P_{\gamma i,e} \times G \times m \times t}$$

Where:

A : is the specific activity of the parent radionuclide or its daughters assuming the secular equilibrium in the test sample (Bq/kg or Bq/L),

$C_{i,e}$: is the net count of radionuclide (i) at γ -energy line (e) in keV,
$\varepsilon_{i,e}$: is the absolute efficiency of the used γ -ray spectrometer,
$P_{\gamma\, i,e}$: is the photopeak intensity (%),
G : is the geometry factor which is equal to unity when all test samples were counted under the same conditions,
m : is the weight of constant sample (kg) and
t : is the counting time in seconds.

Evaluation of the radiological characteristics, the parameters that are determined include radon emanation fraction released (EF), radium equivalent index (Ra-eq) and total absorbed dose rate ($D_{\gamma r}$) for the test samples.

To determine the radon (^{222}Rn) emanation fraction released (EF), the waste samples were initially counted (C_1) for 2 h after sealing the sample container, and counted again (C_2) after reaching the radioactive equilibrium between ^{222}Rn decayed from ^{226}Ra and its respective short-life daughters. The ^{222}Rn EC was determined using the formula [20,21]:

$$EF = \frac{N}{A_0 + N}$$

Where ^{222}Rn EF is the radon emanation fraction; A_0 is the amount (net count rate, cps) of ^{222}Rn existing at the sealing time of the sample container; N is the amount of (net count rate, cps) of ^{222}Rn emanated at the radioactive equilibrium.

To represent the activity levels of the materials containing ^{226}Ra, ^{232}Th and ^{40}K, 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 [22,23]:

$$\text{Ra-eq (Bq/kg)} = A_{Ra} + 1.43\, A_{Th} + 0.077\, A_K$$

Where: A_{Ra}, A_{Th} and A_K are the activities (Bq/kg) of ^{226}Ra (^{238}U-series), ^{232}Th and ^{40}K, respectively.

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 (^{226}Ra, ^{232}Th and ^{40}K) were calculated based on guidelines provided by UNSCEAR [24,25]. Therefore, $D_{\gamma r}$ in outdoor air at 1 m above the ground was calculated as follows:

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

2. TE-NORM in petroleum industry

In this part, the waste generated from oil and gas production that were investigated in Egypt and other countries are reviewed. The waste samples namely, Scales, sludge and produced water have been characterized.

2.1. TE-NORM in scales and sludge

The activity concentration of ^{226}Ra in the TE-NORM waste at three different sites for petroleum and gas production in Egypt has been determined using gamma spectroscopy. **El Afifi et al.** [26] chose three sites of oil and gas production for radiological assessment; (1) in the South Sinai Governorate, (2) in the Suez Gulf area, (3) in the Matrouh Governorate. Seven waste samples with an intermediate structure (mixed between granular and massive) were taken from Abu Rudeis (AR) onshore oil and gas field in the Suez Gulf. Nine samples representing two waste types were from Gabal El Zeit (GEZ) offshore oil and gas field at the Suez Gulf. Four samples had a granular structure and 5 samples had a massive one. Eighteen samples with granular structure were taken from Badr El Din (BED) offshore oil and gas field, respectively (Fig. 4). The TE-NORM waste samples taken for analysis, are a mix of scale and sludge formed in the production equipment and removed during the periodical maintenance. The samples were taken from the TE-NORM waste stacks accumulated around the petroleum and gas plants using a stainless steel template of 25×25 cm^2 with a thickness of 5 cm.

The results showed that the average activity concentrations of ^{226}Ra changed between 5.9 and 68.9 kBq/kg (dry weight) in the waste samples from GEZ and AR fields, respectively. In Gabal El Zeit field (GEZ), granular and massive wastes were investigated. The lower activity concentrations (28.6 kBq/kg) of ^{226}R were found in granular samples (GS), while higher values (56.6 kBq/kg) were found in the massive samples (MS). The activity concentrations of ^{226}Ra in all investigated waste samples from different region in Egypt can be ordered as follows: AR > BED > GEZ.

The mean activity concentrations of ^{232}Th were 25.4, 2.6, 7.2 and 61.3 kBq/kg and those of ^{40}K were 1.3, 0.96, 2.3 and 5.9 kBq/kg, for AR, GEZ (GS), GEZ(MS), and BED TE-NORM waste samples, respectively [26]. The lower ^{226}Ra activity concentration in the waste samples may be due to the lower Ra content in the subsurface formation. Therefore, the quantity of ^{226}Ra leached by oil and gas during exploration was lower in this case. Generally, the variation in the ^{226}Ra activity concentrations in TENORM wastes of different origins, can attributed to the differences in the Ra/Ba ratio in the formation waters scale and/or sludge formation processes on the exterior surfaces of the casing material and the amount of ^{226}Ra in the subsurface [19]. The Ra content depends on the amount of Ra present in subsurface formation, formation water chemistry, extraction and treatment processes and the age of the waste after production.

The average ^{222}Rn emanation fraction released from the TE-NORM wastes investigated ranged from 0.053 to 0.081 in the massive samples (MS) from GEZ field and the granular samples (GS) from BED field, respectively. The ^{222}Rn EF released from MS is lower than that of GS although the activity concentration of ^{226}Ra in the MS is higher. The variation of EF is independent of the ^{226}Ra content and is strongly correlated to the grain surface density [7,8,19]. The smaller the grain size the higher the EF [26].

The main types of scale encountered in oil & gas facilities are sulphate scale which results from drilling clay, it called Barite slurry. It is usually colorless or milky white, but can be

almost any color, depending on the impurities trapped in the crystals during their formation. Barite is relatively soft, measuring 3-3.5 on Mohs' scale of hardness. It is unusually heavy for a non-metallic mineral. The high density is responsible for its value in many applications. Barite slurry is generally used as mud in drilling oil. Barite is chemically inert and insoluble. Radium is chemically similar to barium (Ba), strontium (Sr) and calcium (Ca), hence radium co-precipitates with Sr, Ba or Ca scale forming radium sulphate, radium carbonate and – in some cases – radium silicate. The mixing of seawater, which is rich in sulphate, with the formation water, which is rich in brine, increases the scaling formation tendency. Also the sudden change in pressure and temperature or even acidity of the formation water, as it is brought to the surface, contributes to scale build-up. This phenomenon has significant implications for the production of oil; in this case the capacity of the pipe to transfer oil would be reduced significantly. The activity concentration of ^{226}Ra and ^{228}Ra in hard scales in Egypt and some other countries are mentioned in Table 2.

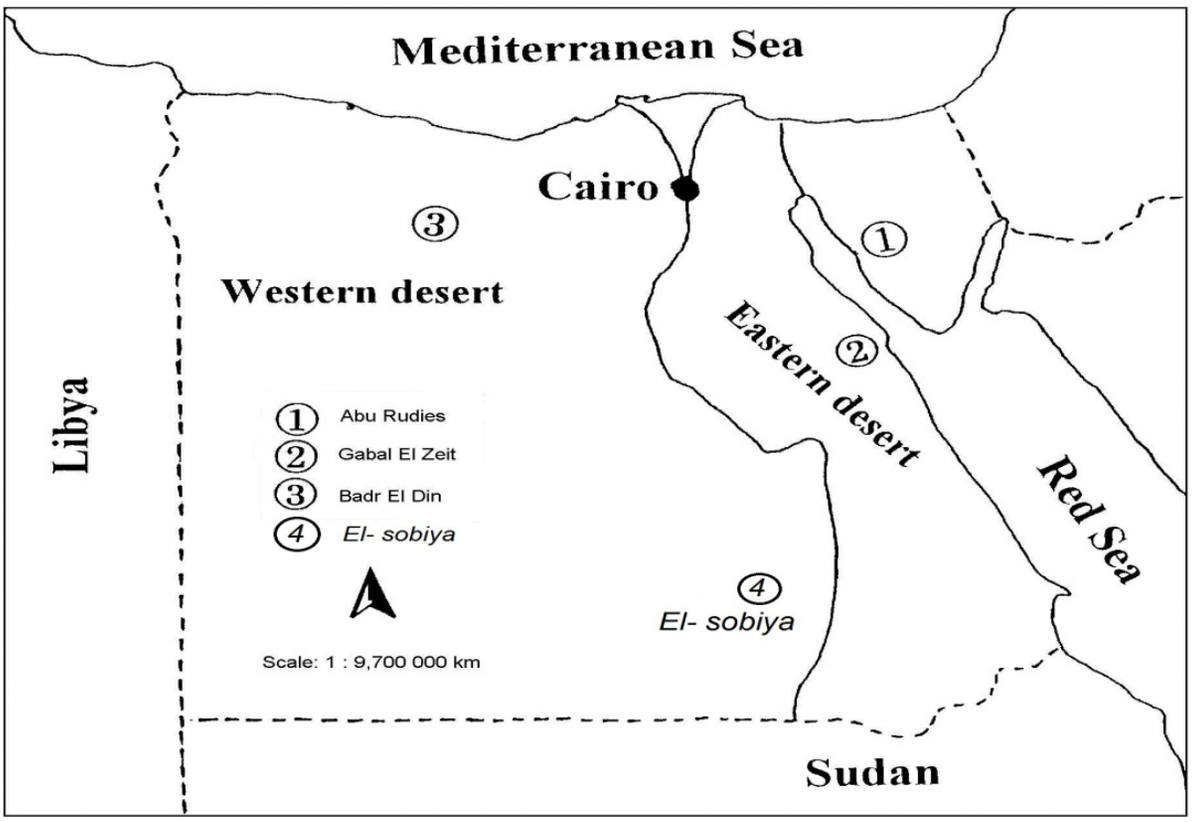

Figure 4. Map for some sites of the TE-NORM wastes associated with phosphate and petroleum and gas production in Egypt.

El Afifi and Awwad [27] characterized TE-NORM from Abu Rudeis region (onshore oil field, Suez gulf area) in the North Sinai Governorate, Egypt. The mineralogical analysis by X-ray techniques (XRF and XRD) has been carried out. Table 3 represents the chemical analysis of the TE-NORM waste samples using the XRF technique. The data showed major elements (Si, Fe, Al and Na) and alkaline earth elements (Mg, Ca, Sr and Ba) [27].

Country/region	Activity (Bq/g)		Ref.
	^{226}Ra	^{228}Ra	
Egypt/oil field			
Abu Rudeis	68.9	24	[27]
Gabal El Zeit	14.8	4.3	[28]
Badr El Din	31.4	43.3	[28]
Red Sea	195	897.8	[29]
Western desert	59.2	244.5	[29]
South Sinia	6.99	1-1.9	[30]
South Sinia	506	32-50	[30]
Other countries			
Australia	20-70		[31]
USA	70.8		[21]
Algeria	1-950		[32]
Tunisia	4.3-658		[33]
UK	1-1000		[6]

Table 2. Activity of ^{226}Ra (U-series), and ^{228}Ra (U-series) in the TE-NORM in Egypt and some other countries [6, 21, 27-33].

Sample code	Concentration (%)							
	Mg	Ca	Sr	Ba	Na	Al	Fe	Si
B.F.[a]	2.44	13.53	0.91	3.25	4.13	3.63	27.12	44.05
A.F.[b]								
F2 (0.1–0.2) mm	2.51	17.94	0.69	2.14	3.82	4.66	29.15	48.75
F4 (0.3–0.5) mm	1.93	11.23	1.27	4.63	4.22	3.67	29.69	44.33
F6 (1.0–1.6) mm	1.53	7.78	1.53	5.47	4.00	3.76	29.96	47.21
F8 (2.0–2.6) mm	1.31	8.65	1.66	6.37	4.58	3.91	27.61	47.39

[a]: TE-NORM waste in its original state (before fractionation).

[b]: After fractionation.

Table 3. Results of XRF analysis of the TE-NORM waste before fractionation and after sieve fractionation for some selected fractions [27].

The radioactivity of naturally occurring radionuclides of ^{238}U, ^{235}U, ^{232}Th-series and ^{40}K in the sediment samples of the TE-NORM waste from Abu Rudeis region before fractionation (B.F.) and after fractionation (A.F.) are given in Table 4. The bulk waste was fractionated into nine homogeneous fractions with different particle sizes (< 3.0– < 0.1 mm) to show the effect of particle size on the activity distribution. Moreover, radiation hazardous indices including the radium equivalent activity (Ra-eq), radon (^{222}Rn) emanation coefficient (EC) and absorbed dose rate (Dγr) were also estimated of TE-NORM waste. The radon emanation coefficient (EC) is a very important radiological index used to evaluate the amount of the 222Rn emanated fraction released from the waste materials containing naturally occurring radionuclides (e.g. ^{238}U, ^{235}U and ^{226}Ra). In this study, the assessment of Rn EC is related only

to ^{222}Rn decayed from its parent ^{226}Ra content in the waste. Since ^{222}Rn and its respective decay progenies (e.g. ^{210}Pb and ^{210}Po) have longer half lives than that of other radon isotopes, ^{222}Rn is considered to be more radiological hazardous to human health than radionuclides coming from other radon isotopes. Fig. 5 represents the ^{222}Rn EC released from the bulk TE-NORM waste and the different fractions. The amount of the ^{222}Rn fraction emanated from the bulk waste was 0.066. It is found that the grain size has an effect on the amount of ^{222}Rn EC. There is a gradual increase in the ^{222}Rn EC with the waste particle size. This was observed in fine particle sizes from less than 0.1 mm up to 2 mm. In this range, ^{222}Rn EC increased from 0.041 to 0.086. There is no effect of the waste particle sizes on the ^{222}Rn EC released from large particle sizes as shown in the grain sizes between 2 and 3 mm. The radon EC found in this range of particle sizes was ranging between 0.093 and 0.095 [27].

Reported levels of the ^{226}Ra and ^{228}Ra activity concentrations observed in the solid scale and sludge in different countries are listed in Table 5.

Sample	^{238}U-series			^{235}U-series	^{232}Th- series			^{40}K (Bq/g)
	^{238}U (Bq/g)	^{226}Ra (Bq/g)	^{210}Pb (Bq/g)	^{223}Ra (Bq/g)	^{228}Ac (Bq/g)	^{212}Pb (Bq/g)	^{208}Tl (Bq/g)	
B.F.	7.1	86.9	4.4	2.7	24.0	22.4	25.2	1.3
A.F.*								
F1	7.5	60.4	4.3	3.5	25.8	24.7	22.9	1.9
F2	4.5	43.0	4.2	1.7	19.1	17.0	20.3	1.1
F3	6.2	55.4	4.3	2.6	21.5	21.0	20.5	1.3
F4	9.2	81.1	5.3	3.7	34.6	33.3	36.5	2.5
F5	11.2	96.5	4.3	5.2	41.4	37.2	39.0	3.4
F6	9.6	85.4	4.4	3.5	39.7	36.2	40.1	3.6
F7	7.1	78.3	4.5	4.0	35.4	36.4	32.9	4.3
F8	11.8	102	6.5	5.7	43.7	38.5	39.0	4.8
F9	7.1	54.5	2.7	3.4	22.8	20.1	22.1	2.5

* F1 (< 0.10) mm, F2 (0.1–0.2) mm, F3 (0.2–0.3) mm
F4 (0.3–0.5) mm, F5 (0.5–1.0) mm, F6 (1.0–1.6) mm
F7 (1.6–2.0) mm, F8 (2.0–2.6) mm, F9 (2.6–3.0) mm

Table 4. Results of gamma-spectrometric analysis of the TE-NORM waste before (B.F.) and after (A. F.) dry fractionation [27].

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. ^{238}U and ^{232}Th series, and/or ^{40}K. Values of Ra-eq activity for the bulk TENORM waste and the waste fractions were calculated. It is clear that Ra-eq exceeds the maximum permissible radium activity (Ref. value is 370 Bq/kg) as reported by Zaidi et al. [23]. The higher Ra-eq activity reached about 164.9 kBq/kg in fraction F8, whilst the lower value amounted 70.4 kBq/kg in F2 (Fig. 6). The higher the radioactivity level in the waste, the higher is the radiological impacts, especially when considering the potential of operators to be exposed via internal contamination by ingesting the dust during waste processing. The total absorbed dose rate

due to g-emissions was estimated and the obtained values are presented in Fig. 6 [27]. It is recommended that the acceptable total absorbed dose rate by the workers in areas containing g-radiations from ^{238}U and ^{232}Th series and their respective decay progenies, as well as ^{40}K, must not exceed 0.055 mGy/h [24]. It is obvious that the calculated total absorbed dose rates for all waste samples are higher than the recommended dose level that are acceptable (Fig. 8). The low total absorbed g-dose rate is 31 mGy/h in fraction F2, while the high value is 72.7 mGy/h in fraction F8. It is clear that the absorbed dose rate depends on the activities of g-emitters (e.g. ^{226}Ra, ^{232}Th ^{40}K), while it is independent of the waste particle size. Therefore, the total absorbed dose rates increases with the activity concentration, and consequently enhances the radiological impact on the workers surrounded by the wastes.

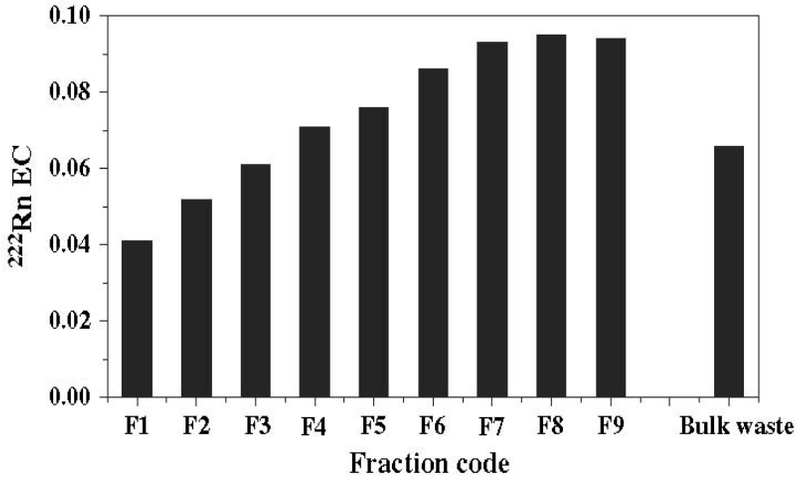

Figure 5. Effect of the waste particle size on the radon emanation fraction release on TENORM of petroleum in Egypt.

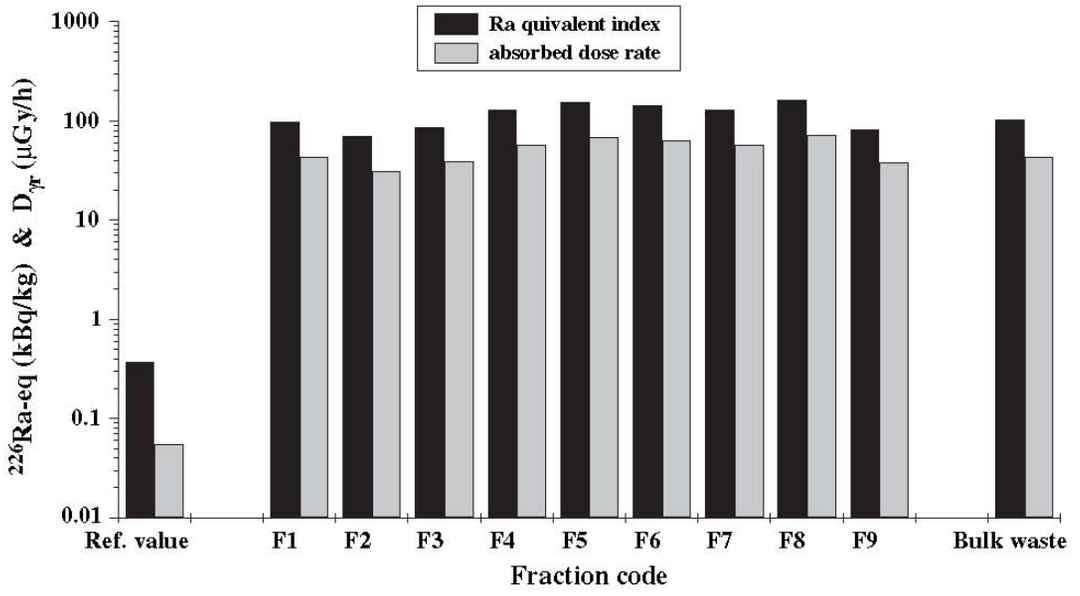

Figure 6. Variation of radium equivalent index and total absorbed dose rate with waste fractions and bulk Waste of TENORM of petroleum in Egypt.

Field	Sample	^{226}Ra (Bq/kg)	^{228}Ra (Bq/kg)
Algeria [32]	Scale	1000-950.000	
Australia [34]	Scale	21.000-250.000	48.000-300.000
Brazil [35]	Scale	19.100-323.000	4210-235.000
Brazil [36]	Scale	121.000-3.500.000	148.000-2.195.000
Brazil [37]	Scale	77.900-2.110.000	101.500-1.550.000
Congo [38]	Scale	97-151	
Egypt [27]	Scale	68.900	24.000
Egypt [29]	Scale	7541-143.262	35.460-368.654
Egypt [30]	Scale	493-519	32-50
Italy [38]	Scale	< 2.7-2890	
Kazakhstan [39]	Scale	510-51.000	200-10.000
Malaysia [40]	Scale	114.300-187.750	130.120-206.630
Norway [41]	Scale	300-32.300	300-33.500
Saudi Arabia [42]	Scale	.08-1.5	
Tunisia [38]	Scale	31-1189	
Tunisia [33]	Scale	4300-658.000	
UK [6]	Scale	1000-1.000.000	
USA [43]	Scale	up to 3.700.000	
USA [21]	Scale	15.400-76.100	
Australia [34]	Sludge	25.000	30.000
Brazil [35]	Sludge	50.000-168.000	49.000-52.000
Brazil [36]	Sludge	< LLD-413.000	< LLD-117.900
Egypt [29]	Sludge	18.000	13.250
Egypt [30]	Sludge	5.27-8.68	1-1.9
Malaysia [40]	Sludge	6-560	4.520
Norway [41]	Sludge	100-4700	100-4600
Tunisia [38]	Sludge	66-453	

Table 5. Ranges of activity levels of ^{226}Ra in different scale and sludge samples

As shown in Table 5, the concentration levels of radium nuclides in scale vary within a wide range being much higher than those of the sludge. According to the latest Environmental Protection Agency (EPA) estimation, the average radium nuclide concentration is around 18,000 Bq/kg and 2800 Bq/kg in scale and sludge, respectively [44]. Elevated concentration activities of both radionuclides, exceeding the exemption level of 10,000 Bq/kg recommended by IAEA safety standards, were frequently found in the scale samples. A large uncertainty is observed in the estimations of the total amount of radioactive waste generated by oil industry, and the EPA assumes that 100 tons of scale per oil well are generated annually in the United States [44], while for the North Sea wells a somewhat lower value of 20 t is suggested [45] and only 2.25 t per year by one oil-producing well for Latin American oil producing countries [46]. It was also estimated that approximately 2.5×10^4 and 2.25×10^5 tons of contaminated scale and sludge, respectively, were generated each year from the petroleum industry in the middle of the previous decade [47,48]. This means

that TENORM waste from the oil industry may generate radiation exposure levels which require attention and continuous monitoring during some routine operation in this industry. This exposure is caused by external radiation coming from the ^{226}Ra radionuclide and its progenies: ^{214}Pb and ^{214}Bi as well as by inhalation of α -emitting radionuclides: ^{222}Rn as well as ^{218}Po and ^{214} Po formed from ^{222}Rn escaping into the air adjacent to scale deposits, as reported in Table 6.

Country	Reported range (μSv/h)
Algeria [32]	Back Ground-100
United Kingdom [32]	10-300
Egypt [27]	50-100
Congo, Italy, Tunisia [38]	0.1-6
USA [49]	up to300

Table 6. Exposure rate levels in the oil industry

2.2. TE-NORM in produced water

Oil and gas reservoirs contain water (formation water) that becomes produced water when brought to the surface during hydrocarbon production. Oil reservoirs can contain large volumes of this water whereas gas reservoirs typically produce smaller quantities. In many fields, water is injected into the reservoir to maintain pressure and / or maximize production. In many offshore oil fields sea water is additionally injected to maintain pressure, and it mixes with the formation water. In such cases, in the exploited oil/water mixture, the content of the production water can reach even 95%. For this reason, the produced waters are typically saline and rich in Cl^- anions forming aqueous complexes with Ra that enhance the mobility of Ra nuclides from adjacent geological rocks into these waters [50]. Comprehensive older literature reviews of radium nuclide concentrations in formation and produced water indicated an average radium nuclide concentration in waters in excess of 1.85 Bq/dm3 and exceptionally up to ~ 1000 Bq/dm^3 [49,51,52]. As ^{226}Ra originated from the radioactive decay of ^{238}U, while ^{228}Ra from ^{232}Th, the $^{226}Ra/^{228}Ra$ ratio in the oil-field brines depends on the U/Th ratio of the reservoir rock and ranges from 0.1 to 2.0, but for the most cases its activities are comparable.

Typical ranges or average values of the radium radionuclide concentrations in the formation or produced water from different oil fields, including the recent data, are listed in Table 7 [29,32,34,38,51,53-62].

A critical review of the intense studies of the activity concentrations of ^{226}Ra, ^{228}Ra as well as ^{210}Pb and ^{210}Po in produced water in 2003 from Norwegian oil and gas platforms located in the North Sea were also reported [55]. The concentrations of ^{226}Ra and ^{228}Ra in produced water discharged from these offshore platforms vary between 0.1 Bq/dm^3 and about 200 Bq/dm^3 with the average values estimated to be 3.3 Bq/dm^3 and 2.8 Bq/dm^3, respectively. Slightly higher radium activities ~ 10 Bq/dm3 have been found for produced water outfalls in the Gulf of Mexico [63]. The European Commission (EC) derived the specific clearance levels at low activity for metals and buildings in radiation protection. The world wide

average concentration of these radionuclides in produced water discharged to the environment is estimated at 10 Bq/l. These concentrations are approximately three orders of magnitude higher than natural concentrations of radium in drinking or sea water. Because the radium radionuclide concentrations in that waste water are usually below the clearance levels (Table 8), it is recognized as a low specific activity waste and they may be injected into underground formations or disposed into the sea.

Field	Sample	^{226}Ra (Bq/dm^3)	^{228}Ra (Bq/dm^3)
Algeria [32]	Formation water	5.1-14.8	
Australia [34]	Produced water	17[a]	23[a]
Brazil [53]	Produced water	0.01-6	0.05-12
Congo [38]	Produced water	5.1[a]	
Egypt [29]	Formation water	5-40	1-59
Italy [38]	Produced water	0.2-2	
Norway [54]	Formation water	0.3-10.4	
Norway [55]	Produced water	3.3[a]	2.8[a]
Norway [56]	Produced water	0.5-16	0.5-21
Syria [57]	Produced water	9.9-111.2	8.8-60.4
UK [58]	Produced water	1.7[a]	
USA [51]	Produced water	0.1-60	
USA [59]	Produced water	0.15-21.6	0.7-1.7
USA [60]	Oilfield brine	12.6[a]	15.1[a]
USA [61]	Produced water	22-30	25-30
Egypt [62]	Produced water	26.5-217.5	
	Crude oil	31-2669	

[a] Mean activity concentration.

Table 7. Ranges of activity levels in produced water from the oil fields

Radionuclide	Concentration (Bq/g)
^{40}K	100
^{226}Ra	10
^{232}Th	1

Table 8. The European Commission Clearance levels.

A comprehensive evaluation of discharges from the oil industry to the sea was done for European waters during the European Commission Marina Project [64].

The annual release of ^{226}Ra and ^{228}Ra with produced water from off-shore fields in Europe in the 1990s stabilized at around 5 and 2.5 TBq per year, respectively. The commonly used two steps model of the radionuclide dispersing and diluting in the water in the vicinity of the oil platforms predicts a diluting factor up to 10^3 within minutes and within a few meters of the discharge source [65]. Therefore, additional radium nuclide concentrations in seawater of the local zone could be estimated as equal to around 5–10 Bq/m^3, in comparison with the

natural concentration of around 1 Bq/m^3 for ^{226}Ra. The radium activities in the produced water for the North Sea, a yearly release of 0.65 TBq for ^{226}Ra and 0.33 TBq for ^{228}Ra was appraised for offshore oil production from Argentina and Brazil [66].

Produced water contains a complex mixture of inorganic (dissolved salts, trace metals, suspended particles) and organic (dispersed and dissolved hydrocarbons, organic acids) compounds, and in many cases, residual chemical additives (e.g. scale and corrosion inhibitors) that are added into the hydrocarbon production process. Feasible alternatives for the management and disposal of produced water should be evaluated and integrated into production design. These alternatives may include injection along with seawater for reservoir pressure maintenance, injection into a suitable offshore disposal well, or export to shore with produced hydrocarbons for treatment and disposal. If none of these alternatives are technically or financially feasible, produced water should be treated before disposal into the marine environment. Treatment technologies to consider include combinations of gravity and / or mechanical separation and chemical treatment, and may include a multistage system, typically including a skim tank or a parallel plate separator, followed by a gas flotation cell or hydrocyclone. There are also a number of treatment package technologies available that should be considered depending on the application and particular field conditions. Sufficient treatment system backup capability should be in place to ensure continual operation and for use in the event of failure of an alternative disposal method, for example, produced water injection system failure. Where disposal to sea is necessary, all means to reduce the volume of produced water should be considered, including:

- Adequate well management during well completion activities to minimize water production;
- Recompletion of high water producing wells to minimize water production;
- Use of down hole fluid separation techniques, where possible, and water shutoff techniques, when technically and economically feasible;
- Shutting in high water producing wells. To minimize environmental hazards related to residual chemical additives in the produced water stream, where surface disposal methods are used, production chemicals should be selected carefully by taking into account their volume, toxicity, bioavailability, and bioaccumulation potential [67].

The average worldwide activity levels of uranium (U) , thorium (Th) and potassium (K) [68] and the exemption activity levels of NORM as recommended in the IAEA basic safety standards [69], were given at Tables 9&10. The average worldwide levels of the most common radiological indices [68] was given at Table 11. These indices include radium equivalent (Ra-eq), total absorbed dose ($D_{\gamma r}$) and effective annual dose rate (EDAR).

Radionuclide	U	Th	K
Activity level (Bq/Kg)	50	50	500

Table 9. The average worldwide activity levels of U, Th and K [68].

Radionuclide	^{238}U	^{226}Ra	^{222}Rn	^{232}Th	^{228}Ra	^{224}Ra
Exemption level (Bq/g)	1	10	10	1	10	10

Table 10. The exemption activity levels of NORM as recommended in the IAEA basic safety standards [69].

Radiological indices (Unit)	Ra-eq (Bq/Kg)	$D_{\gamma r}$ (nGy/h)	EADR (mSv/yr) for worker	EADR (mSv/yr) for Public
Activity level (Bq/Kg)	370	55	20	1

Table 11. The average worldwide levels of the most common radiological indices [68].

2.3. Investigation of TE-NORM treatment in petroleum industry

In the last decade, attention was focused on the environmental and health impacts from the uncontrolled release of TENORM wastes [19,28,70,71]. Therefore, the treatment of these wastes is of increasing interest because accumulation of large amounts with a significant activity may cause a health risks to the workers through exposure, inhalation of radon (^{222}Rn) decayed from radium and/or ingestion of waste dust during the periodical maintenance of the equipment used. The trials towards the treatment of TENORM wastes from many industries are still limited. In this concern, removal of ^{226}Ra from TENORM wastes produced from oil and gas industry was carried out by a simple extraction process using saline solutions (i.e., seawater) and chemical solutions [70]. The chemical treatment process of TE-NORM sludge has been carried out by suspending the clay fraction content in the solid waste in suitable leaching solutions was reported. It was found that, the maximum removal % of ^{226}Ra is ~ 85% [70]

El-Afifi, studied the treatment of radioactive waste containing ^{226}Ra from oil and gas production, using different chemical solutions, in terms of a simple and sequential techniques based on suspending ^{226}Ra through the clay fraction in the waste. More than 50% of ^{226}Ra was removed through the treatment using moderate acids and salts solutions, while more than, 75% of ^{226}Ra was removed based on successive treatment or using some strong chelating reagent solutions [28].

The development of the treatment of a sludge TENORM waste produced from the petroleum industry in Egypt, using selective leaching solutions based on two approaches 'A' and 'B' has been investigated by El-Afifi et al. [71]. The results obtained showed that treatment of the waste through main four successive leaching steps removed ~ 78 and 91% of ^{226}Ra, 65 and 87% of ^{228}Ra as well as 76 and ~ 90% of ^{224}Ra using approaches A and B, respectively [71]. El-Afifi et al. [72] reported some data about the radiological characterization for phosphogypsum waste and phosphate rocke samples by γ -ray spectrometer. El-Didamony et al.[73] used the solvent extraction technique in treatment of phosphogypsum waste obtained as a byproduct of phosphoric acid production from phosphate ore.

3. Conclusion

The naturally occurring radioactive materials (NORM) are found everywhere. We are exposed to it every day. NORM represent an integral part of the planet, our bodies, the food we eat, air we breath, the places where we live and work, and within products we use. However , in the exploration and extraction processes of oil and gas, the natural radionuclides ^{238}U, ^{235}U and ^{232}Th, as well as the radium-radionuclides (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) and ^{210}Pb,.etc., are brought to the slurry surfaces and may contain levels of radioactivity above the surface background. The petroleum waste (scale or sludge) have been produced by two mechanisms: either incorporation or precipitation onto the production equipment such as: pipelines, tank storage, pumps, ..etc. The waste generated in oil and gas equipment is due to the precipitation of alkaline earth metals as sulfate, carbonates and/or silicates. It is clear that PG and sludge and scale wastes represent one of the major sources of ^{226}Ra in the environment. Since the concentration of ^{226}Ra found in both of them waste exceeds that permitted by the international regulations, it was found necessary to reduce the risks due to indoor radon and direct γ -radiation in each wastes to be used in different life aspects.

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Appendix

Nomenclature of symbols associated with this article is listed as follows.

NORM	Naturally occurring radioactive material
TE-NORM	Technically enhanced naturally occurring radioactive material
$t_{1/2}$	Half-life
hr	Hour
min	Minute
y	Year
α	Alpha decay
β	Beta decay
γ	Gamma decay
dpm	Disintegration per minute
g	Gram
Ci	Curie
mSv	Milly sievert
Γ	Gamma constant can be used to determine radiation dose

USEPA	United state of Environmental protection agency
Bq	Becquerel
AR	Abu Rudeis region
GEZ	Gabal El Zeit region
BED	Badr El Din region
cm	Centimeter
GS	Granular samples
MS	Massive samples
EF	Emanation fraction released
XRF	X ray fluorescence
XRD	X ray diffraction
B.F.	Before fractionation
A.F.	After fractionation
F	Fraction
mm	Milie meter
Ra-eq	Radium equivalent activity
Dγr	Absorbed dose rate
mGy	Gray
IAEA	International Atomic Energy Agency
UNSCEAR	United Nations Scientific Committee on the Effects of Atomic Radiation
WHO,	World Health Organization
Kg	Kilo gram
u	Combined uncertainty
CV	Coefficient variance
SD	Standard deviation
TDS	Total dissolved solids
EC	Electric conductivity
A_0	Net count rate of ^{222}Rn existing at the sealing time of the sample
N	Net count rate of ^{222}Rn emanated at the radioactive equilibrium

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