Abstract: Recent concern has been devoted to the hazard arising from Naturally Occurring Radioactive Material scales (NORM) which are omnipresent in the earth's crust. These scales contain mainly $^{226}$Ra and its daughter products, which can cause an exposure risk. Fifteen petroleum scales samples were collected at different Oil fields in the Red Sea Refineries (Company) for Petroleum Services in the Eastern Desert of Egypt were investigated. The specific radio activities of $^{238}$U, $^{232}$Th, $^{226}$Ra, $^{40}$K, and its daughter nuclide for all samples were determined using high-resolution gamma-ray spectrometry. The radium equivalent activity, radiation hazard indices and absorbed dose rate in air for all waste samples were estimated. The radon emanation coefficient of the waste samples and the radon exhalation rate was estimated. Its values equal 0.341547312 gm m$^{-3}$ and 0.011153571 (111.5 $\times$ 10$^{-4}$ Bqm$^{-2}$·s$^{-1}$) respectively. The gamma ray dose rates, with the associated occupational doses in the samples, and $^{226}$Ra concentration in hard/soft scale samples were determined. The chemical structure of the waste samples was investigated using X-ray florescence technique (XRF) and Sr, Ca, Fe, Ba, Si, Pb, K, Zn, S, Ti, and Mn were found in all samples. From this study, it was noticed that the concentrations of the natural radionuclides in the petroleum scales samples were higher than that of the petroleum sludge samples exceeds the NRC limits. Results obtained are discussed and compared with the international recommended data.

Keywords: NORM, Petroleum, Radiation exposure, Natural Radioactivity, Waste, Gamma-ray spectroscopy, Scale, Sludge , Radon.

1. Introduction

Radioactive materials which occur naturally and expose people to radiation occur widely, and are known by the acronym 'NORM'. NORM is an acronym for Naturally Occurring Radioactive Material, which includes all radioactive elements found in the environment. Long-lived radioactive elements such as uranium, thorium and potassium.

In 1998, an attention was given to the health impacts from the uncontrolled release of naturally occurring radioactive materials (NORM) wastes on concentrated and accumulated in tubing and surface equipment in the form of scale, sand and sludge [Rood, 1998]. In the exploration and extraction processes of oil and gas, the natural radionuclides $^{238}$U, $^{232}$Th and $^{40}$K, as well as the radium- radionuclides ($^{226}$Ra, $^{224}$Ra, $^{228}$Ra and $^{228}$Ra) and $^{210}$Pb, etc., are brought to the slurry surfaces and may contain levels of radioactivity above the surface background [API, 1992; Rood, 1998, 2001; Shawky et al., 2001; Matta et al., 2002; Al-Masri and Suman, 2003; Godoy and Crux, 2003; Hamlat et al., 2003; Mohamad Puad and Muhd Noor, 2004; Omar et al., 2004; El Afifi and Awwad, 2005; Gazineu et al., 2005]. As these materials are handled, their radioactive Constituents may be separated, resulting in NORM waste [Testa et al., 1998]. Nuclear spectroscopic analysis showed that the main radionuclides present in NORM waste associated with petroleum industries are $^{238}$U, $^{232}$Th and $^{40}$K series and any of their decay products, such as radium and radon are example of NORM. Radon is a radioactive gas; therefore it follows the general gas law and the theory of radioactivity. Radon has two aspects; it induces significant health hazards to uranium miners and people living in normal buildings. Lung cancer is the principal concern associated with radon exposure [Tanner, 1980 and UNSCEAR, 1988]. Radon itself is not responsible for the hazard. Being chemically inert, it does not accumulate to a great degree in the body. Therefore, the primary concern is associated with the short–lived decay products of radon. These species are chemically reactive and so may be deposited on respiratory tract tissues when inhaled may damage cells near the deposition site, contributing to increase the risk of lung cancer [Nazaroff 1992]. The radon concentration inside the container was continuously detected by an Alpha Guard radon monitor (Genitron Instruments GmbH. Co. Frankfurt am Main Germany) for 67 hours see (Fig. 5). These elements have always been present in the Earth's crust and within tissues of all living beings. The philosophy of radiation is to limit NORM locations to a minimum and to concentrate
contaminated equipment/waste into one area such as
the NORM storage. NORMS in the Petroleum Industry
are present in components of both petroleum
production facilities and natural gas production
facilities. The mineralogical analysis by X-ray
techniques (XRF) indicated the incorporation and co-
precipitation of these radionuclides with the alkaline
earth metals (e.g. Mn, Ca, Sr, and Ba) and some
quantities of lead sulphate, carbonate and/or silicate
[Shuller et al., 1995]. This work was necessary since
no studies have been carried out on radioactive levels
in petroleum scales and wastes in Egypt and published
data are not available. The present study includes the
determination of the activity concentrations of the \( {^{238}}U \),
\( {^{226}}R\)a, and \( {^{40}}K \) content in the petroleum scales and
wastes in Egypt City Refinery. The radium equivalent
activity, radiation hazard indices, Annual Effective
Dose \( \mu \)Sv and absorbed dose rate in air for all waste
samples were estimated. The radon emanation
coefficient of the waste samples was estimated. The
chemical structure of the waste samples was
investigated using X-ray florescence analysis (XRF)
with the exempt concentration levels given by the
IAEA [IAEA, 1988, 1994].

2. Material and Methods

Fifteen petroleum scales samples were collected at
different Oil fields in the Red Sea Refineries
(Company) for Petroleum Services in the Eastern
Desert of Egypt, Egyptian General Authority for
Petroleum Resources, Ministry of Petroleum. The
Scale and Sludge samples put into clean containers.
Sample were stored for 30 days before its counting
radioactivity to \( {^{232}}R\)a period to achieve the secular
equilibrium \( \lambda_R \approx \lambda_A \) between radium and its products
and then measure the samples 3600 sec. The energy
and intensity of various gamma-ray lines have been
measured using a system consist of Canberra coaxial
High-Purity Germanium detector (HPGe) which has a
photo peak efficiency of 70% . The energy resolution
of 2 keV Full-Width at Half Maximum (FWHM) for
the 1332 keV gamma-ray line of \( {^{60}}Co \). A cylindrical
lead shield of 5 cm thickness, which contains inner
concentric cylinder of Cu with thickness of 10 mm,
was used to shield the detector and to reduce the effect
of background. The detector was cooled to liquid
nitrogen temperatures and coupled to a PC-based 8K
multichannel analyzer and an ADC with Genie 2000
for data acquisition and analysis. The calibration of the
detector was carried out by using standard point
sources \( {^{60}}Co \) (1173.2 and 1332.5 keV), \( {^{133}}Ba \) (356.1
keV), \( {^{137}}Cs \) (661.9 keV) and \( {^{22}Na \) (1368.6keV) besides
\( {^{222}}R\)a (186.2keV). Absolute efficiency calibration
curves are calculated for activity determination of the
sample by using standard \( {^{222}}R\)a, contained in the same
cylindrical bottles as the samples. The samples were
prepared with a uniform geometry. An empty bottle
with the same geometry was measured for subtracting

Geological Origin

U and Th are present in the earth’s crust at an
average concentration of 4.2 and 12.5 ppm,
respectively [Wollenberg and Smith, 1990]. When a
geochemical formation containing \( {^{238}}U \) and \( {^{232}}Th \) has not
been disturbed (closed system) for more than a million
years, the members of the individual decay series will
have the same activity (Bq/kg) which is known as
secular equilibrium. However, when the geological
formation is not closed to radionuclide migration, \( {^{226}}R\)a
can migrate and be deposited somewhere outside the
formation. Then secular equilibrium will not exist and
the growth of \( {^{226}}R\)a by radioactive decay of its
ancestors will not occur. \( {^{226}}R\)a is said to be
unsupported. See the average radium, uranium,
thorium and potassium content in sedimentary rocks
[NCRP, 1975]. Oil is formed by thermal cracking of
organic matter (kerogen) trapped in sedimentary rock.
As oil migrates, naturally occurring radionuclides
(NORs) may be taken up in the up flowing fluid stream
and may be transferred into connate waters, which may
be produced with oil as production water. During
thermal cracking of kerogen, uranium or thorium
remain with the residual organic matter and they will
not be leached in a reducing environment into passing
fluids. Radium will not leach into a hydrocarbon phase,
but it may leach into the aqueous phase [Bloch and
Key, 1981]. In this work, NORs in scale/sludge
originating from oil fields in the western desert and the
Red Sea region have been characterized and compared
with the exempt concentration levels given by the
IAEA [IAEA, 1988, 1994].
the background. The gamma-ray transitions of energies 1120.3 keV ($^{214}$Bi) and 1764 keV ($^{214}$Bi) were used to determine the concentration of the $^{238}$U series. The gamma-ray transitions of energies 911.1 keV ($^{228}$Ac) and 2614 keV ($^{208}$Tl) were used to determine the concentration of the ($^{232}$Th) series. The 1460 keV gamma-ray transition of $^{40}$K was used to determine the concentration of $^{40}$K in the samples as shown in Table (1) and their intensities. The spectra of the samples were perfectly analyzed using a special PC Genie 2000 software to calculate the concentrations of $^{238}$U, $^{232}$Th and $^{40}$K and their decay products.

2.1. Gamma-Ray Spectrometer System

The instrumentation used to measure γ-rays from radioactive samples consists of a HPGe semiconductor detector, associated electronics, and a computer-based multichannel analyzer [Verma, 2007] as shown in Fig. (1)

Fig.1: Blocked diagram of HPGe γ-ray spectrometer system.

2.2. Sample Collection and Preparation

Samples were collected from different places in one of the work sites of Egyptian Petroleum location. Each sample, 50-400g, was packed in a plastic container, sealed well and stored for 30 days before analysis this allow the in-growth of uranium and thorium decay products and prevent the escape of radiogenic gases $^{222}$Rn and $^{220}$Rn and allow secular equilibrium of $^{238}$U and its decay products see Table (1).

Table (1): The natural radionuclides, their gamma lines used and their intensities [VIENNA, 1990].

<table>
<thead>
<tr>
<th>Parent Nuclide</th>
<th>Max. Activity According to (UNSCEAR)</th>
<th>Daughter Nuclide</th>
<th>γ-ray energy (keV)</th>
<th>Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}$U</td>
<td>130 Bq/Kg</td>
<td>$^{228}$Ra</td>
<td>186.2</td>
<td>3.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{212}$Pb</td>
<td>295.2</td>
<td>18.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{212}$Pb</td>
<td>351.9</td>
<td>35.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{214}$Bi</td>
<td>609.3</td>
<td>45.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{214}$Bi</td>
<td>1120.3</td>
<td>14.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{214}$Bi</td>
<td>1764.5</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{214}$Bi</td>
<td>2204.1</td>
<td>5.0</td>
</tr>
<tr>
<td>$^{232}$Th</td>
<td>85 Bq/Kg</td>
<td>$^{212}$Pb</td>
<td>238.6</td>
<td>45.0</td>
</tr>
<tr>
<td>$^{232}$Th</td>
<td></td>
<td>$^{206}$Tl</td>
<td>583.1</td>
<td>30.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{225}$Ac</td>
<td>911.1</td>
<td>29.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{228}$Ac</td>
<td>968.6</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{208}$Tl</td>
<td>2614.7</td>
<td>36.0</td>
</tr>
<tr>
<td>$^{40}$K</td>
<td>1600 Bq/Kg</td>
<td></td>
<td>1460</td>
<td>10.67</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Natural specific activity measurement

The activity levels for radionuclides in the measured samples are computed using the following equation [Amrani 2001]

$$ A = C_R / \epsilon(E) \ int \gamma \ W $$  \hspace{1cm} (1)

Where:

$A$ = The activity level of a certain radionuclide (Bq/kg)
\( C_R = \) The net count rate of the sample (counts / seconds)
\( \varepsilon(E) = \) The detector efficiency for the specific gamma ray energy
\( I_\gamma = \) The intensity of gamma-line in a radionuclide
\( W = \) The dried sample weight in kg.

Activities due to the presence of \(^{226}\)Ra, \(^{232}\)Th and \(^{40}\)K radionuclides have been determined in the samples. The minimum, maximum and mean activity values of \(^{226}\)Ra, \(^{232}\)Th and \(^{40}\)K found in these samples are listed in Table 2. As may be seen in this table the measured values of activity in the samples due to \(^{232}\)Th vary from 34339 Bq kg\(^{-1}\) to 427 Bq kg\(^{-1}\), \(^{226}\)Ra activities vary from 285823 Bq kg\(^{-1}\) to 66 Bq kg\(^{-1}\) and variation in \(^{40}\)K activities ranges from 1031 Bq kg\(^{-1}\) to 51 Bq kg\(^{-1}\).

The activity concentration is shown in Table 2 where all activity is very higher than world average except value.

**Table 2**: Minimum, maximum and mean activity concentration values for scales and sludge samples.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Minimum (Bq / kg)</th>
<th>Maximum (Bq / kg)</th>
<th>Medium (Bq / kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Scales</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{238})U</td>
<td>9140</td>
<td>285823</td>
<td>147481.5</td>
</tr>
<tr>
<td>(^{232})Th</td>
<td>427</td>
<td>34339</td>
<td>17383</td>
</tr>
<tr>
<td>(^{40})K</td>
<td>51</td>
<td>1031</td>
<td>541</td>
</tr>
<tr>
<td><strong>Sludge</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{238})U</td>
<td>66</td>
<td>1567</td>
<td>816.5</td>
</tr>
<tr>
<td>(^{232})Th</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(^{40})K</td>
<td>787</td>
<td>1544</td>
<td>1165.5</td>
</tr>
</tbody>
</table>

For \(^{238}\)U activity concentration was determined by measuring the 295.2 keV (18.7 %) and 351.9 keV (35.8.1 %) gamma-rays from \(^{214}\)Pb and the 609.3 keV (45%) and 1120.3 keV (14.9%) gamma-rays from \(^{214}\)Bi. \(^{232}\)Th activity was determined from the gamma-rays of 238.6 keV (45 %) from \(^{215}\)Pb and 338.4 keV (12 %), 911.1 keV (29 %) and 968.6 keV (17.5 %) from \(^{228}\)Ac and 583.1 keV (30 %) gamma-rays from \(^{208}\)Tl. \(^{40}\)K concentration was measured from its 1460 keV (10.67 %) gamma-ray line.

The obtained spectrum of the background gamma radiation was subtracted from the measured gamma ray spectra of the samples. The characteristic gamma-ray emitters are marked above the corresponding peaks.

A selected one of the obtained spectrum for sample is shown in Figs. 2, 3 and 4.
To assess the radiological hazard of the scales sample, it is useful to calculate an index called the radium equivalent activity, \( Ra_{eq} \), defined according to the estimation that 1 Bq / kg of \(^{226}\)Ra, 1.43 Bq / kg of \(^{232}\)Th and 0.077 Bq / kg of \(^{40}\)K produce the same \( \gamma \)-ray dose [Amrani, 2001]. This index \( Ra_{eq} \) is given as:

\[
Ra_{eq} = A_{Ra} + 1.43 A_{Th} + 0.077 A_{K}
\] (2)

Where \( A_{Ra} \), \( A_{Th} \) and \( A_{K} \) are the activity concentration in Bqkg\(^{-1}\) of \(^{226}\)Ra, \(^{232}\)Th and \(^{40}\)K, respectively. The maximum value of \( Ra_{eq} \) in petroleum scales samples must be less than 370 Bq kg\(^{-1}\) for safe use [UNSCEAR, 1993], i.e., to keep the external dose below 1.5 mSv y\(^{-1}\). The values of \( Ra_{eq} \) are higher this criterion limit. In petroleum scales samples, the \( Ra_{eq} \) activity are not within the recommended safety limit when used in industry.

The calculated values of the radium equivalent \( Ra_{eq} \) for the studied petroleum scales samples are given in Table 3.

Another radiation hazard index, the representative level index, \( I_{\gamma r} \), used to estimate the levels of \( \gamma \)-radiation hazard associated with the natural radionuclides in specific samples, is defined as [KAFALA, 2007].

\[
I_{\gamma r} = (A_{Ra} / 150) + (A_{Th} / 100) + (A_{K} / 1500)
\] (3)

Where \( A_{Ra} \), \( A_{Th} \) and \( A_{K} \) are the activity concentrations in Bq/kg of \(^{226}\)Ra, \(^{232}\)Th and \(^{40}\)K respectively. The values of \( I_{\gamma r} \) for the studied samples are given in table 3. It is clear that the studied samples exceed the upper limit for the representative level which is unity.

### Table (3): Activity Concentrations of \(^{238}\)U, \(^{232}\)Th and \(^{40}\)K, Radium equivalent activity (Bqkg\(^{-1}\)), External Annual dose (mSv/y), Gamma-Radiation external and internal hazard (\( I_{\gamma r}, H_{in} \)), Absorbed dose (nGy/h) and the Annual Effective Dose (\( \mu \)Sv).

<table>
<thead>
<tr>
<th>Sample code</th>
<th>(^{238})U (Bq/kg)</th>
<th>(^{232})Th (Bq/kg)</th>
<th>(^{40})K (Bq/kg)</th>
<th>Dose Rates nGy/h(( \mu )Sv)</th>
<th>Ra equiv.</th>
<th>EAD (( \mu )Sv)</th>
<th>( H_{in} )</th>
<th>( I_{\gamma r} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15152</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6471</td>
<td>15152</td>
<td>0.0684</td>
<td>95.899</td>
</tr>
<tr>
<td>2</td>
<td>172563</td>
<td>6769</td>
<td>1031</td>
<td>-</td>
<td>78209</td>
<td>181712.847</td>
<td>0.8157</td>
<td>1118.520</td>
</tr>
<tr>
<td>3</td>
<td>86060</td>
<td>6216</td>
<td>657</td>
<td>-</td>
<td>40892</td>
<td>94440.029</td>
<td>0.4222</td>
<td>568.820</td>
</tr>
<tr>
<td>4</td>
<td>66</td>
<td>-</td>
<td>1103</td>
<td>-</td>
<td>75</td>
<td>150.931</td>
<td>0.0007</td>
<td>0.647</td>
</tr>
<tr>
<td>5</td>
<td>240</td>
<td>-</td>
<td>787</td>
<td>-</td>
<td>136</td>
<td>300.599</td>
<td>0.0014</td>
<td>1.683</td>
</tr>
<tr>
<td>6</td>
<td>9140</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3915</td>
<td>9140</td>
<td>0.0413</td>
<td>57.848</td>
</tr>
<tr>
<td>7</td>
<td>595</td>
<td>-</td>
<td>1544</td>
<td>-</td>
<td>320</td>
<td>713.888</td>
<td>0.0033</td>
<td>4.087</td>
</tr>
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<td>0.0484</td>
<td>66.273</td>
</tr>
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<td>-</td>
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<td>-</td>
<td>135</td>
<td>316</td>
<td>0.0014</td>
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<td>-</td>
<td>32</td>
<td>77</td>
<td>0.0003</td>
<td>0.487</td>
</tr>
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<td>12954</td>
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<td>-</td>
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<td>118382.36</td>
<td>0.5258</td>
<td>689.408</td>
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<tr>
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<td>15</td>
<td>285823</td>
<td>34339</td>
<td>-</td>
<td>-</td>
<td>144778</td>
<td>331837.26</td>
<td>1.4753</td>
<td>1941.589</td>
</tr>
</tbody>
</table>

### 3.2. Radiation Hazard Index

This factor is used to estimate the level of gamma radiation hazard associated with natural radionuclides in specific petroleum scales samples. The external hazard index is obtained from \( Ra_{eq} \) expression through the assumption that its maximum value allowed (equal to unity) corresponds to the upper limit of \( Ra_{eq} \) (370 Bqkg\(^{-1}\)) according to UNSCEAR, 1993. This index value must be less than unity in order to keep the radiation hazard insignificant; then, the internal hazard index (\( H_{in} \)) can be defined also as the potential radiological hazard posed by the different samples was calculated using the following equation [Ngachina, 2007],

\[
H_{in} = (A_{Ra} / 185) + (A_{Th} / 259) + (A_{K} / 4810)
\] (4)
Where $A_{Ra}$, $A_{Th}$ and $A_{K}$ are the specific activities of $^{226}Ra$, $^{232}Th$ and $^{40}K$ (in Bq.kg$^{-1}$) were calculated for the investigated samples to indicate different levels of external $\gamma$-radiation due to different combinations of specific natural activities in specific petroleum scales samples.

3.3. External Annual Dose

The external annual effective dose (EAD) is calculated for a room with dimensions of $4 \times 5 \times 2.8$ m, estimated that the samples is put. The equation used to calculate the annual effective dose may be defined as [Ngachina, 2007 and Hussain et.al, 2010] The external annual effective dose (EAD) is calculated,

$$EAD = (0.92 A_{Ra} + 1.1 A_{Th} + 0.08 A_{K}) \times 10^{-9} \text{ (Gy/h)} \times (0.7 \text{ Sv/Gy}) (24 \times 365 \times 0.8 / y) \quad (5)$$

Where, 0.92, 1.1 and 0.08 are the specific dose rates of $Ra$, $Th$ and $K$, respectively; with an estimated indoor occupancy factor of 0.8.

The variation of the activity concentration (Bq/kg) of $U$, $Th$ and $K$ radionuclides in the collected samples in location of Petroleum Company is represented in Table (3).

The absorbed dose in tissues are calculate using the conversion factor in (nGy/h), which are Known to be

$$C_{K} = 0.0437 \text{ for } K, \quad C_{Th} = 0.662 \text{ for } Th \quad \text{and } C_{U} = 0.427 \text{ for } U$$

The equivalent dose rate is calculated according to the equation:

$$D = R_{U} C_{U} + R_{Th} C_{Th} + R_{K} C_{K} \quad (6)$$

Where $R_{U}$, $R_{Th}$, and $R_{K}$ are the conversion factors expressed in activity of $^{238}U$, $^{232}Th$ and $^{40}K$ in Sv/h

$$R_{U} = 0.427, \quad R_{Th} = 0.662 \quad \text{and } R_{K} = 0.0437$$

$C_{U}$, $C_{Th}$ and $C_{K}$ are the specific activity of $^{238}U$, $^{232}Th$ and $^{40}K$ respectively expressed in Bq/kg.

Figure (2- 4) for sample code 2, 3 and 15 show the spectrum of the energy lines for $^{238}U$, $^{232}Th$ and $^{40}K$ from their decay products $\gamma$-lines energy.

The $U$-283, Th-232 and K-40 in NORM samples activity concentration values reported in this study are higher than the international recommended limits.

3.5. Radon Emanation Coefficient and Radon Exhalation Rate of the Waste Samples (Active Method)

The active method for measuring radon exhalation rate is carried out in Zagazig University, Faculty of Science, Physics Department by using the pulse type ionization chamber (Alpha Guard, Genitor Instruments, Frankfurt, Germany). Alpha Guard was calibrated in Egyptian National Institute for Standard. Each sample and Alpha Guard monitor were placed together at the same time in the Alpha Guard chamber as shown Fig. 6. Alpha Guard chamber is a container consisting of a firm corrosion-resisting stainless steel container with a removable gas-tight lid. The container dimensions were 45.0 cm diameter and 31.7 cm height. Its volume was 50.4 liters. The lid was equipped with three gas-tight electric ducts. One duct server, together with a special charger, was used as a power supply for the radon analyzer or monitor. The second duct was used to connect the fan in the middle of the inner side of the lid to the power supply, by means of a power adapter. The fan was used to ensure an even distribution of the radon exhalation from the sample in the interior of the container. The third duct provided communication between the Alpha Guard in the interior of the container and an external PC. The concentration of radon emanated from each sample inside the exhalation container was allowed to build up with time and, was measured in every one hour in diffusion mode of Alpha Guard monitor system to avoid thoron gas concentration effect for an average time of 3 days.

Fig. (5): Radon growth curve for sample code number 2 as an example.

For the Alpha Guard (diffusion mode), the sensitivity for thoron is about 10% of radon sensitivity [ISHIKAWA, 2004]. Moreover, the typical petroleum samples show the radium concentration is higher than thorium. Even if we assume the radon and thoron exhalation rate are the same, the effects of thoron on measured concentrations can be neglected. A direct
measurement of radon concentration for each sample is obtained. Alpha Guard was used to measure the radon concentration at a time t during the growth of radon inside the chamber. From the radon concentration, the equilibrium concentration of radon for each sample (the saturated constant radon concentration in the sealed space which is the expected concentration at t >30 days) can be estimated. The radon exhalation rate of any sample, is defined as the flux of radon released from the surface of material, was also calculated.

Fig. (6): Active technique set up for measuring radon exhalation rate.
To determine the radon ($^{222}$Rn) emanation coefficient (EC), the samples code number 2 were initially counted for 3 days, and counted again 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 described by [White and Rood, 2001; El Afifi and Awwad, 2005].

$$^{222}\text{Rn (EC)} = \frac{N_{\text{Rn}} \cdot m}{N_{\text{Ra}} \cdot V}$$  

(7)

$$E = \frac{N_{\text{Rn}} \cdot V \cdot \lambda}{\text{sample surface area}}$$  

(8)

where $^{222}$Rn (EC) is the radon emanation coefficient, $N_{\text{Rn}}$ is the equilibrium Radon concentration (6940 ± 92 Bq), $N_{\text{Ra}}$ is the Radium concentration, (172563 Bq), $\lambda$ is radon decay constant ($2.1 \times 10^{-6}$ s$^{-1}$), $V$ is the Sample volume (0.011775 m$^3$), $m$ is the mass sample (85gm) and $E$ is the radon exhalation rate. The value of Rn(Ec) and $E$ from equation 7, 8 is equal to 0.341547312 gm m$^{-3}$ and $111.5 \times 10^{-4}$ Bq m$^{-2}$ s$^{-1}$ respectively.

3.6. XRF analysis

Table (4) and Fig. (7), represents the analysis of the waste petroleum samples using the XRF technique. The data showed major elements (Sr, Ba, Si, Pb, K, Zn, S, and Ti) and alkaline earth elements (Mn and Ca) as well as trace amounts of Fe in all the samples.

<table>
<thead>
<tr>
<th>Element</th>
<th>ms</th>
<th>Sigma</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>9.2928</td>
<td>0.9662</td>
<td>9284</td>
</tr>
<tr>
<td>S</td>
<td>1.4606</td>
<td>0.2263</td>
<td>3686</td>
</tr>
<tr>
<td>K</td>
<td>3.6806</td>
<td>0.6623</td>
<td>5239</td>
</tr>
<tr>
<td>Ca</td>
<td>42.7984</td>
<td>0.5323</td>
<td>70639</td>
</tr>
<tr>
<td>Ti</td>
<td>1.4246</td>
<td>0.4729</td>
<td>2358</td>
</tr>
<tr>
<td>Mn</td>
<td>0.5073</td>
<td>0.2631</td>
<td>1453</td>
</tr>
<tr>
<td>Fe</td>
<td>21.1092</td>
<td>0.2374</td>
<td>67435</td>
</tr>
<tr>
<td>Zn</td>
<td>0.7863</td>
<td>0.1878</td>
<td>4049</td>
</tr>
<tr>
<td>Sr</td>
<td>6.7239</td>
<td>0.1279</td>
<td>84388</td>
</tr>
<tr>
<td>Rh</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ba</td>
<td>10.8879</td>
<td>1.2263</td>
<td>12739</td>
</tr>
<tr>
<td>Pb</td>
<td>1.3285</td>
<td>0.3149</td>
<td>7841</td>
</tr>
<tr>
<td></td>
<td>~100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. (7): Illustrates the analysis in one of the petroleum scales sample by XRF Technique

4. Conclusions

An investigation was carried out to find out the concentration of Naturally Occurring Radioactive Materials (NORMs) in petroleum scales samples which collected at different Oil fields in the Red Sea Refineries (Company) for Petroleum Services in the Eastern Desert of Egypt. Activity concentrations of $^{238}$U, $^{232}$Th and $^{40}$K in scales and sludge generated during oil extraction and production operations were determined using an HPGe gamma spectrometric system. Concentrations ranged from 66 to 285823 Bq kg$^{-1}$ for $^{238}$U, 427 to 34339 Bq kg$^{-1}$ for $^{232}$Th and 51 to 1031 Bq kg$^{-1}$ for $^{40}$K. The magnitude of these results demonstrates the need of screening oil residues for their radionuclide content in order to decide about their final disposal. While NORM-contaminated equipment has been a concern in the Red Sea Refineries (Company) for Petroleum Services in the Eastern Desert of Egypt well drilling, the results of this investigation show that NORM contamination of Egypt equipment is significant. Egypt well drilling equipment and wastes constitute a health risk for the country residents a potential degradation of the country environment. From the present results, it may be concluded that, for different samples NORM around location of petroleum companies, the level of natural radioactivity and hazard parameters are higher than the international recommended limits.

A recommendation that risks should be reduced to account for lower-dose-rate exposures:

- The workers at oil fields are the most threatened. Therefore, they should be classified as occupationally radiation workers.
- Such workers should follow approved radiation protection regulations and receive regular medical surveillance.
- The sites of NORM activities require qualified radiation protection experts to safeguard workers and environment from exposure and
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