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Natural Radioactivity in the Petroleum Waste from Iraqi Refinery

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Abstract - The present study aimed to measure the natural radioactivity present in the crude oil and oil waste of Iraqi refinery. The specific activities in (19) samples of crude oil and oil waste from Dora and Bijie refineries in Iraq were measured using gamma spectrometry technique, with high purity germanium detector (HPGe). The results show that two radionuclides (^{214}Bi, ^{214}Pb) belonging to the ^{238}U series, three radionuclides (^{208}Ti, ^{212} Bi, ^{212} Pb) belonging to ^{232}Th series, one natural radionuclide (^{40}K), and one artificial radionuclide (^{137}Cs) were detected. For Dora refinery, solid samples, D1-D8, the average specific activities ^{214}Bi, ^{214}Pb were 11.7 , 21.9 Bqkg^{-1}, the average specific activities of ^{208}TI, ^{212}Bi, ^{212}Pb were 11.9 , 6.8, 8.6 Bqkg^{-1}, the average specific activity of ^{137}Cs was 1.3 Bqkg^{-1}, the average of specific activity of ^{40}K was 147 Bqkg^{-1} and for liquid samples D9-D12, the average specific activities ^{214}Bi, ^{214}Pb were 0.5, 2.4 Bql^{-1}, radionuclides ^{208}TI, ^{212}Bi, ^{212}Pb, ^{137}Cs were not appeared and the average specific activities of ^{40}K was 4.0Bq^{-1}. For Bijie refinery solid samples J1-J5, the average of specific activities of ^{214}Bi and ^{214}Pb were 0.8, 2.2 Bqkg^{-1}, the average specific activities of ^{212}Bi and ^{212}Pb were 0.2 , 0.1 Bqkg^{-1}, the average of specific activity of natural radionuclide ^{40}K was 2.9 Bqkg^{-1} and for liquid samples the average specific activities ^{214}Bi, ^{214}Pb were 0.5, 2.4Bq^{-1} ,the radio nuclides, ^{208}TI, ^{212}Bi, ^{212}Pb and ^{137}Cs were not appeared in Bijie samples.

Keywords: Crude oil, NORM, sludge, Scale, Petroleum.

I. INTRODUCTION

The oil extraction and production industry generates several types of solid and liquid waste, scales, sludge, and water. There are typical residues found in such facilities which are likely to be contaminated with Naturally Occurring Radioactive Material (NORM). As a result of oil processing, the natural radionuclides can be concentrated in such residues, called Technologically Enhanced Naturally Occurring Radioactive Material (TENORM) [1]. TENORM wastes associated with oil and gas operations at the oil fields occur in the form of scale deposits, sludge and water generated during operations.

Scales formed by precipitation, as well as sludge, which accumulates in the bottom of storage tanks, and other equipment contain variable amounts of the naturally occurring radionuclides from the ^{238}U and ^{232}Th series besides ^{40}K. The main radionuclides concentrated in scales and sludge during the production of oil and gas are ^{226}Ra and ^{228}Ra [2-4]. Scales buildup may cause problems in the operation of an installation by clogging tubing and valves, thus restricting the flow. Radionuclides are known to be associated with organic materials in nature. Therefore, oil, gas and oil field brines frequently contain radioactive materials [5]. These materials accumulate in piping used to remove, transport and process petroleum and natural gas. Emphasis was given to the quantification of ^{226}Ra and ^{40}K since these radionuclides is responsible for most of the external exposure in such facilities [6-7]. Gamma spectrometry system used in this study is a fully integrated data acquisition and computation system comprising of high purity germanium detector, preamplifier, amplifier, multi channel analyzer (MCA), Bias high voltage power supply (0-5000 cps). Personal computer is used as (MCA) [8-9].

II. MATERIALS AND METHODS

The details of samples of scale and sludge taken from Al-Dora and Bijie refineries are shown in Table I. The oil waste and crude oil samples taken from the refineries were stored for one month under normal

laboratory conditions, which is necessary to get a radiological equilibrium.

Table I: The types and locations of samples

Sample code	State type	Location of samples
D_1	solid – sludge	oil waste from al-sudanya
D_2	solid-scale	oil waste from (heavy products)
D_3	solid – sludge	oil waste from (light products)
D_4	solid – sludge	oil waste around pit abandonment
D_5	solid – sludge	oil waste from (Hi-tech)
D_6	solid-brines	oil waste from beside of furnace
D_7	solid – sludge	depleting area of crude oil
D_8	solid-sediment	refining dep. down of furnace
J_1	solid-sludge	vacuum residue produces from RC
J_2	solid – scale	extract from heavy metal from RC
J_3	solid – scale	foam wax heavy metal from RC
J_4	solid-sludge	oil waste from storage tank
J_5	solid – scale	Asphalt
D_9	liquid-scale	reached crude oil from Kirkuk
D_{10}	liquid-scale	reached crude oil from Basrah
D_{11}	liquid-scale	oil waste from (pit abandonment)
D_{12}	liquid-scale	Reduce crude oil (RC)
J_6	liquid-scale	Crude oil
J_7	liquid-scale	RC

The activity concentrations of the radionuclides in the samples were measured using a High Purity Germanium Detector. The gamma spectrometry system consists of an n-type (EG & G ORTEC) of 17% relative efficiency having a resolution of 2 keV at 1332 keV and coupled to a 4096 channel multi-channel analyzer (MCA). The detector mounted in a cylindrical lead shield (100 mm thick) to reduce the background radiation.

The background spectra were used to correct the net peak area of gamma rays of the measured isotopes. The energy and efficiency calibration were performed using a reference standard solution of Europium -152 Figure 1. One kilogram of each solid sample and one liter of each liquid sample was taken in a standard marinelli beaker and counted 1080 second. The activity concentration of ^{226}Ra was evaluated from the energies of 351.92keV of ^{214}Pb and 609.31keV of ^{214}Bi, respectively. Similarly, the activity concentration of ^{232}Th was determined from the energies of 583.19keV of ^{208}Tl, 1080keV of ^{214}Bi and 238.6KeV of ^{212}Pb. This was based on the assumption that secular equilibrium has been established between the long-lived parent radionuclide's ^{238}U and ^{232}Th, and their short lived daughter radionuclide's. The activity concentration of ^{40}K was determined from the energy of 1460.83keV. The expression used for the calculation of the activity concentrations is given by the following equation in Bq/kg [6]:

$$\text{Activity (Bq kg}^{-1}) = \frac{cps}{\varepsilon * w * I_{\gamma}} \quad (1)$$

Where cps: is the net counts/s under the photo peak of interest,

ε: is the counting efficiency,

I_γ: relative intensity of gamma emission at energy considered,

W: is the mass of the sample (kg).

The external dose from NORM in the oil waste from the oil locations was calculated by using the following equation [10]:

$$H(t) = A_x \times DRF \quad (2)$$

Where,

H (t): The external dose rate at time (t), nGy/h.
A_x : The specific activity of radionuclide of the sample, Bq/kg.
DRF: The dose rate conversion factor.
DRF for Th-232 series = (0.623) nGy/h per Bq/kg.
DRF for U-238 series = (0.461) nGy/h per Bq/kg.
DRF for K-40 = (0.0414) nGy/h per Bq/kg.

III. RESULTS AND DISCUSSION

The specific activities for the radionuclide's for twelve solid samples of scale and sludge from Dora and Bijie refineries were shown in Table II. The radionuclides detected in this study include: ^{214}Bi, and ^{214}Pb belong to the ^{238}U series, and radionuclides ^{212}Bi, ^{212}Pb, and ^{208}Tl belonging to ^{232}Th series, one natural radionuclide - ^{40}K, and one artificial radionuclide ^{137}Cs.

For Dora refinery, solid samples, the average of specific activities of ^{214}Bi, ^{214}Pb were 11.7±10.4 and 21.9±23 Bq/kg respectively, the average of specific activities of ^{208}Tl, ^{212}Bi, ^{212}Pb were 11.9±7.8, 6.8±4.7 and 8.6±5.3 Bq/kg, the average of specific activity of artificial radionuclide ^{137}Cs was1.3±1.7Bq/kg and the average of pecific activities of natural radionuclide, ^{40}K was 147±40 Bq/kg.

The highest concentrations for ^{214}Pb, ^{208}TI were 79 and 32.31 Bqkg^{-1} respectively in sample D_8 (solid sediment), Figure 2, for ^{137}Cs 5.20 Bqkg^{-1} in sample D_2 (solid scale), and for ^{40}K, 189.3Bqkg^{-1} in sample D_7 (solid –sludge). The radionuclides, i.e., ^{212}Bi, ^{226}Ra, ^{208}Tl, ^{212}Bi, ^{212}Pb and ^{137}Cs were not appeared in liquid samples, the average of specific activities of natural radionuclide ^{40}K was 4.0±2.0Bqkg^{-1}.

For Bijie refinery, solid samples, the average of specific activities of ^{214}Bi, ^{214}Pb were 0.8±0.8, 2.2±0.7 and ^{212}Bi 0.2 Bqkg^{-1} respectively and for natural radionuclide ^{40}K 2.9±1.5, the radionuclides, i.e., ^{208}Tl, ^{212}Bi, ^{212}Pb and ^{137}Cs were not appeared in solid samples, Figure 3.

For liquid samples, the average of specific activities of ^{214}Bi, ^{214}Pb were 0.5 and 2.4Bq/kg, the radionuclides, i.e., ^{208}Tl, ^{212}Bi, ^{212}Pb and ^{137}Cs were not appeared in liquid samples, the average of specific activities of natural radionuclide ^{40}K was 3.7±1.9Bqkg^{-1}.

The equivalent dose from NORM in the samples from all the oil location was calculated using equation (2), as shown in Table IV.

The lowest exposure rate was 0.05 mSv/y for Bijie refinery samples, and the highest exposure rate was 0.12 mSv/y for Dora refinery. All these values are below the allowed limit from IAEA that was 1 mSv/y for the public [11].

Workers and people that live in oil locations and refineries most likely to be exposed to this source of radiation from oil waste, but production sites can also pose a potential hazard to members of the public.

The radioactive contamination may be present in produced water, drilling mud, or can concentrate in pipes, storage tanks, or other extraction equipment. The contamination may be present in mineral scale, sledges, slimes, or evaporation ponds or pits. The radiation comes from (NORM) in the underground rock and sediment. When companies drill for gas or oil, the produced fluids, including water, may contain radionuclides, primarily radium-226, radium-228, and radon. The radon gas may be released to the atmosphere, while the produced water and mud containing radium are placed in ponds or pits for evaporation, re-use, or recovery.

The reason of the difference in the natural radioactivity for Bije and Dora refinery that the most crude oil of Dora refinery comes from Southern of Iraq which contains a small concentration of uranium.

Table II

The specific activities (Bq/kg) of radionuclide's in solid samples from Dora and Bijie refineries

Sample code	^{214}Bi Bq/kg	^{214}Pb Bq/kg	^{208}Tl Bq/kg	^{212}Bi Bq/kg	^{212}Pb Bq/kg	^{40}K Bq/kg	^{137}Cs Bq/kg
Dora refinery samples							
D_1	6.6	12.6	7.3	3.3	5.5	117.9	BDL
D_2	6.9	20.3	7.1	2.2	5.8	107.6	5.2
D_3	8.4	4.1	9.9	5.6	8.3	178.9	0.7
D_4	8.5	18.6	10.0	6.9	7.9	180.7	BDL
D_5	6.2	14.1	7.6	4.9	5.3	140.6	0.8
D_6	9.0	29.8	11.0	6.1	6.9	184.9	0.5
D_7	8.8	14.5	10.1	6.7	6.7	189.3	0.3
D_8	39.1	79	32.3	18.6	22.5	76.1	0.3
Average	11.7± 10.4	21.9±23	11.9±7.8	6.8±4.7	8.6±5.3	147±40	1.3±1.7
Biji refinery samples							
J_1	BDL	BDL	BDL	BDL	BDL	1.5	BDL
J_2	BDL	BDL	BDL	BDL	BDL	1.7	BDL
J_3	1.9	3.2	BDL	BDL	BDL	5.7	BDL
J_4	0.2	1.5	BDL	0.2	BDL	2.5	BDL
J_5	0.2	2.0	BDL	BDL	BDL	3.1	BDL
Average	0.8±0.8	2.2±0.7	BDL	0.2	BDL	2.9±1.5	BDL

Table III

The specific activities (Bq/l) of radionuclide's in liquid samples from Dora and Bijie refineries

Sample code	^{214}Bi Bq/l	^{214}Pb Bq/l	^{208}Tl Bq/l	^{212}Bi Bq/l	^{212}Pb Bq/l	^{40}K Bq/l	^{137}Cs Bq/l
Dora refinery samples							
D_9	BDL	BDL	BDL	BDL	BDL	5.2	BDL
D_{10}	BDL	BDL	BDL	BDL	BDL	6.7	BDL
D_{11}	BDL	BDL	BDL	BDL	BDL	2.2	BDL
D_{12}	BDL	BDL	BDL	BDL	BDL	1.8	BDL
Average	BDL	BDL	BDL	BDL	BDL	4.0±2.0	BDL

Biji refinery samples							
J_6	0.5	2.4	BDL	BDL	BDL	4.6	BDL
J_7	BDL	BDL	BDL	BDL	BDL	1.8	BDL
Average	0.5	2.4	BDL	BDL	BDL	3.7±1.9	BDL

MDA: Below Detection Limit

Table IV

The dose rate and equivalent dose from NORM in oil locations

oil location	Dose rate (nGy/h)	Equivalent dose rate (mSv/y)
Dora refinery	20.22	0.12
Bijie refinery	6.83	0.05

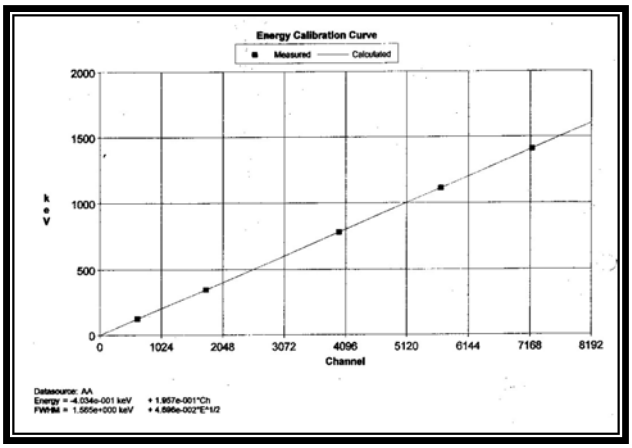

Fig.1. Energy Calibration

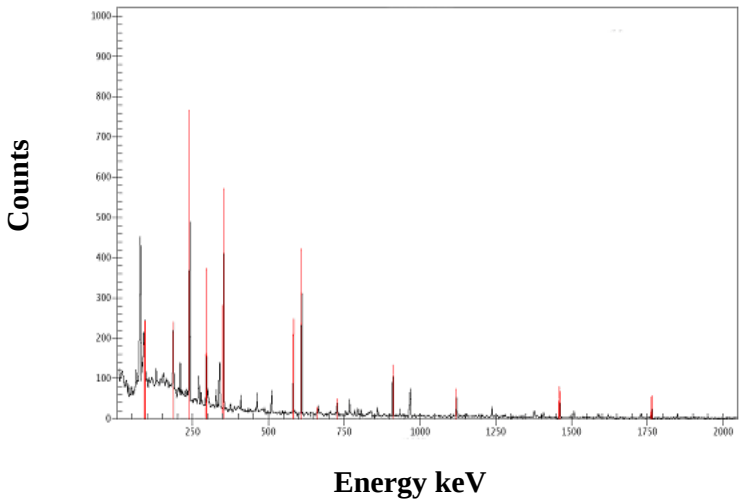

Fig.2: Gamma-rays spectrum for sample (D_8)

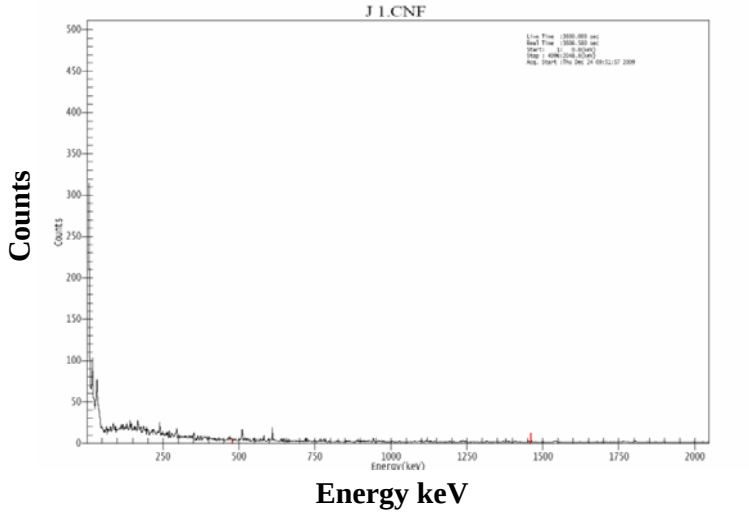

Fig. 3: Gamma-rays spectrum for sample (J_4)

IV. CONCLUSION

The activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the collected samples were determined using high-resolution gamma spectrometry. This study showed that the activity concentrations of natural radionuclides in the collected samples are within the recorded values compared with similar samples studied in other countries. Although the activity concentrations of the selected isotopes are lower than the values recommended by IAEA [11].

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