

ACTIVITY CONCENTRATIONS OF ^{224}Ra , ^{226}Ra , ^{228}Ra AND ^{40}K RADIONUCLIDES IN REFINERY PRODUCTS AND ADDITIONAL RADIATION DOSE ORIGINATED FROM OIL RESIDUES IN TURKEY

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Total of 56 crude oil, refinery product, waste water, sludge and scale samples collected from three refineries were measured by gamma-ray spectrometry. Except for nine samples, all refinery products samples were found below the minimum detectable activity (MDA) values. ^{224}Ra , ^{226}Ra , ^{228}Ra and ^{40}K activity concentrations in crude oil and refinery product samples were measured from MDA values to 11.7 ± 4.5 , 14.9 ± 3.5 , 11.6 ± 4.5 , $248.5\pm 18.5 \text{ Bqkg}^{-1}$ respectively. ^{224}Ra , ^{226}Ra , ^{228}Ra and ^{40}K activity concentrations in scale, sludge and water samples were measured from MDA values to 343.7 ± 11.8 , 809.2 ± 29.0 , 302.5 ± 21.6 , $623.0\pm 80.9 \text{ Bqkg}^{-1}$ respectively. Radium equivalent activities of residue samples were calculated up to $1241.8\pm 42.4 \text{ Bq/kg}$. Maximum activity concentration index and alpha index were found 4.2 and 4.0 respectively. The annual effective doses of four residue samples were calculated equal or above permitted dose rate for public, i.e. 1mSv/y .

INTRODUCTION

^{238}U and ^{232}Th series radionuclides, ^{87}Rb and ^{40}K are called primordial radionuclides and found more or less almost all geological materials like soil, rocks, mines and also fossil fuels. Due to the human activities or shifting sands of presence, aforementioned radionuclides could accumulate certain parts of industrial facilities. Owing to the enhanced concentrations, these materials are often called Technologically Enhanced Naturally Occurring Radioactive Materials (acronym TENORM). Oil and gas production, coal mining and combustion, drinking or waste water treatments, mining and processing metals such as aluminium, copper, iron or gold, fertilizer production and phosphate mining, processing of radio-elements such as uranium, radium, and thorium and without number of industrial processes could produce TENORM or most encountered acronym NORM [1]. Among aforecited industrial processes, oil and gas industry including refinery residues produces higher activity concentration as NORM.

Petroleum containing %83-87 carbon, %11-15 hydrogen and %1-6 sulphur, paraffin, naphthenic and aromatics is a complex mixture of approximately thousands of particular hydrocarbon molecules [2]. Either oil or produced water rise to surface are contain a modicum of natural radionuclides (Table 1.1). ^{238}U and ^{232}Th are major radionuclides of ^{238}U and ^{232}Th decay series. These radionuclides don't migrate from mixture of oil and water reservoir rise up to surface. However ^{226}Ra from the ^{238}U series; ^{224}Ra and ^{228}Ra from the ^{232}Th series are removed via oil and water mixture. Therefore ^{226}Ra , ^{224}Ra and ^{228}Ra are known as

unsupported [4]. ^{238}U and ^{232}Th series radionuclides under certain conditions depend upon temperature, pressure and acidity are accumulated in the component of production processes facility and by-products.

Table 1. Activity concentrations of nuclides [3]

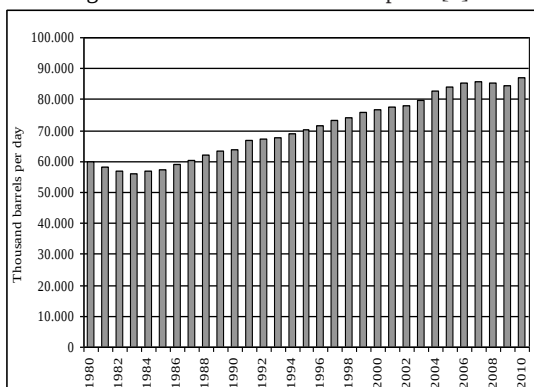
Radionuclide	Produced Water (Bq.l^{-1})	Crude Oil (Bq.kg^{-1})
^{238}U	0.0003-0.1	0.0001-10
^{226}Ra	0.002-1,200	0.1-40
$^{210}\text{Pb}^*$, $^{210}\text{Po}^{**}$	0.05-190*	0-10**
^{232}Th	0.0003-0.001	0.03-2
^{228}Ra	0.3-180	
^{224}Ra	0.5-40	

Almost all crude oil is processed in the oil refinery to generate petrochemical products such as gasoline, diesel fuel, kerosene, jet fuel etc. Recent studies indicated that they could also concentrate in the products and production processes residues most familiar scale and sludge samples in oil refineries. Many researchers have paid special attention either enhanced activity concentration of petrochemical products or production processes residues such as scale, sludge or produced water [5][6]. Enhanced concentrations can cause additional inhalation dose originated from suspended particles or radioactive gaseous especially carrying out maintenance or cleaning of production facility equipment, storage tanks etc. Radionuclides accumulated to the worker's skin or accidentally taken from the NORM containing

residues into the body via digestion can result in skin or ingestion radiation dose. NORM contaminated installation can lead to additional external radiation to the industrial workers or related member of the public.

According to the U.S. Energy Information Administration, world crude oil consumption have increased %45.1 between the years of 1980-2010 given in the Figure 1. Increasing rate indicated that even though various industrial sectors have used to produce energy or kind of industrial products, oil production or processing industry has maintained its importance in all. It is conceivable that the generation amount of scale and sludge residues in processes is directly proportionate to the oil production or processes also oil consumption rate.

Figure 1 World crude oil consumption [7]



In reference to the Basic Safety Standards from the point of the view of the radiation protection aspect, economic and social factors being taken into account, common goal is to keep radiation doses as low as reasonably achievable in all situation including naturally occurring radioactive materials (NORM) related sector's workers and member of the public [8]. In this study for assessment of radiological hazard arising from end products and by-products of oil refining industry were researched. In the point of the view of the radiation protection of workers and member of the public 56 crude oil, refinery products, waste water, sludge and scale samples collected from three refineries were measured by gamma-ray spectrometers. Activity concentrations of ^{226}Ra from the ^{238}U series; ^{224}Ra and ^{228}Ra from the ^{232}Th series and ^{40}K radionuclides were determined by gamma spectrometric method. Considering these results some radiological parameters named radium equivalent activity and annual effective dose of samples were determined and finally results discussed.

MATERIALS AND METHODS

Sampling and sample preparation

Total 56 samples were collected from 3 oil refineries (coded A, B and C) belong to private sector in particular location of Turkey. Initially, background and samples dose rate were measured by portable survey meters has ionization chamber detectors. Then 4 crude oil, 30 refinery product, 5 waste water, 14 sludge and 3 scale samples were collected by metallic sampler and put into 1liter plastic bottles have seal caps or plastic bags each approximately 1-1.5kg with regard to solid or liquid phase. Afterwards all samples were labelled and arranged as motionlessly transport and brought to the Health Physics department of Sarayköy Nuclear Research and Training Centre.

A standard sample preparation procedure was performed for solid scales samples brought to the internal dosimetry laboratory. They were heated in temperature controlled drying oven at 105°C for 6-8 hour to remove moisture. Following, samples were put into cylindrical plastic containers. Plastic analysis containers have 6cm diameter and 5cm high. Then, samples were weighed, hermetically sealed with parafilm and kept for 30 days for secular equilibrium of ^{226}Ra decay products before the measurements.

For liquid refinery products and oily sludge samples standard sample preparation procedures were not applied properly. Plastic analysis containers are containing a small number of organic impurities and oil products affecting container walls and parafilm while samples are waiting for secular equilibrium before the measurements. Thus glass autoclave containers were used for the measurements of aforementioned samples.

Radioactivity Measurement

Radioactivity measurements were performed Gamma Spectrometry Laboratory (GML) accredited by TURKAK (Turkish Accreditation Agency) member of ILAC (International Laboratory Accreditation Cooperation) in 2009. GML has taken part in comparison tests and inspected by TURKAK experts annually since then. Samples were counted with commercially available gamma spectrometry systems equipped with germanium detectors had various relative efficiencies (%10, %40 well type, %70 n-type, %110, %150). Two software programs GAMMAVISION-32 and GENIE-2000 were used for data analyses. One of the spectrometers detector specifications are given as follows: p-type HPGe detector having 451 cm³ active volume, 110% relative efficiency, 85:1 peak-to-compton ratio and 2.1 keV and 1.3 keV energy resolutions at 1332.5 keV of ^{60}Co and 122 keV of ^{57}Co , respectively. To reduce the background, detector installed in front opening split-

top shielding. The shielding is composed of 10cm lead thickness, 9.5mm steel outer housing, 1mm thick tin layer, 1.5mm thick copper layer. Measurement system was equipped with DSA-1000 multichannel analyzer.

Before measurements systems energy calibrations were carried out by using a counted spectrum of standard point sources (^{241}Am , ^{137}Cs , ^{60}Co). Using peaks of counted point sources, energy calibration were performed by the fitting energy curve to an analytical function.

Calculation of efficiency curve (efficiency calibration) of gamma spectrometry system was performed with a spectrum counted a certified radioactive standard volume source has the same distance and geometry. To get free from coincidence summation, IAEA reference materials of RGU-1 (U ore), RGTh-1 (Th ore) and RGK-1 (K_2SO_4) were used. Activity concentrations are directly proportional with the net count rate of the samples. Therefore to determine activity concentrations of samples, net count rate of reference material and net count rate of samples were compared with each other and calculated at 2σ statistical uncertainty. To reduce self-absorption effect, density corrections were performed in order to have same geometry via numerical solution of integral function [9].

The activity concentrations of ^{226}Ra from the ^{238}U series; ^{224}Ra and ^{228}Ra from the ^{232}Th series radionuclides in samples were calculated from gamma-ray photopic of decay products. Due to the interference of ^{235}U energy at 185.7 keV, activity concentration of ^{226}Ra was calculated from 295.2, 351.9 keV gamma-ray energies of ^{214}Pb and 609.3 keV of ^{214}Bi . The activity concentration of ^{228}Ra was calculated from 338.4, 911.2 keV gamma-ray energies of ^{228}Ac and 583.2 keV of ^{208}Tl . The activity concentration of ^{224}Ra was calculated from the 238 keV of ^{212}Pb . The activity concentration of ^{40}K was determined by using its own energy of 1460.8 keV. The contribution of ^{232}Th via its decay product nuclide ^{228}Ac (1459.2 keV peak) near to the 1460.8 keV peak was neglected because of the small contribution while activity concentration of ^{40}K was calculated according to Lavi et al. [10]

Minimum detectable activity (MDA) values were calculated as follows [11]:

$$\text{MDA}(\text{Bqkg}^{-1}) = \frac{F_c \times \sigma_{NB}}{\epsilon \times P \times t \times w} \quad (1)$$

Where F_c is represent statistical coverage factor and equal to 1.64 for %95 confidence level and σ_{NB} symbolize square root of background count number. Symbols given in denominator of equation (ϵ , P , t and w) are represent efficiency of detector, emission probability, measurement time and weight of dried sample in kg respectively.

RESULTS AND DISCUSSION

Activity Concentration of Crude Oil, Waste Water and Refinery products

Activity concentration and statistical uncertainties (2σ) of ^{226}Ra , ^{224}Ra , ^{228}Ra and ^{40}K in crude oil samples were calculated and results given in the table 2. It seems that activity concentration of all oil samples are below of the minimum detectable activity (MDA) value.

Radionuclide content of waste water samples are given in the Table 3. Only 2 water samples have radionuclides. ^{40}K Activity concentration of water-1 sample were observed $39.1 \pm 11.1 \text{ Bqkg}^{-1}$. Water-5 has $4.5 \pm 1.6 \text{ Bqkg}^{-1}$ ^{226}Ra and $47.5 \pm 15.6 \text{ Bqkg}^{-1}$ ^{40}K activity concentration. 3 water samples were found below the minimum detectable activity.

Activity concentration and statistical uncertainties (2σ) of ^{226}Ra , ^{224}Ra , ^{228}Ra and ^{40}K in refinery products were calculated and results given in the Table 4. ^{224}Ra nuclides were observed only in 2 refinery product of Refinery C. ^{226}Ra were found only in 6 samples of Refinery B and C. These are asphalt (3), kerosene (1), naphtha(1) and light diesel fuel (1) samples. ^{228}Ra were found only in 2 (kerosene and mineral oil) samples of Refinery C. ^{40}K were observed in 6 refinery products. Results indicated that there is not any relation between radionuclide content and refinery products.

Table 2. Activity Concentration of Crude Oil Samples

Refinery Code	Sample No	Activity Concentration (Bq kg^{-1})			
		^{224}Ra	^{226}Ra	^{228}Ra	^{40}K
B	1	<1,1	<1,6	<4,8	<10,0
B	2	<1,0	<1,0	<1,0	<1,0
B	3	<4,6	<5,6	<4,6	<10,0
B	4	<1,2	<4,3	<2,1	<11,0

Table 3. Activity Concentration of Waste Water Samples

Refinery Code	Sample	Activity Concentration (Bq kg ⁻¹)			
		²²⁴ Ra	²²⁶ Ra	²²⁸ Ra	⁴⁰ K
B	Water-1	<1,0	<1,3	<1,9	39,1 ± 11,1
B	Water-2	<1,6	<1,1	<1,6	<4,2
C	Water-3	<1,0	<1,0	<1,0	<1,0
C	Water-4	<1,0	<1,0	<1,0	<1,0
C	Water-5	<1,6	4,5 ± 1,6	<1,6	47,5 ± 15,6

Table 4. Activity Concentration of Refinery Products

Table 4: Heavy Concentration of Refinery Products						
Refinery Code	Sample	Activity Concentration (Bq kg ⁻¹)				
		²²⁴ Ra	²²⁶ Ra	²²⁸ Ra	⁴⁰ K	
1.	A	Fuel Oil-1	<5,6	<8,0	<5,6	<10,0
2.	A	Fuel Oil-2	<1,2	<1,4	<1,9	<10,0
3.	B	Fuel Oil-3	<5,7	<8,2	<5,7	<10,0
4.	C	Fuel Oil-4	<1,2	<1,0	<1,9	248,5 ± 18,6
5.	C	Fuel Oil-5	<2,4	<1,2	<2,4	<14,7
6.	A	Diesel Fuel-1	<10,0	<10,0	<10,0	<10,0
7.	C	Diesel Fuel-2	<1,0	<1,0	<1,0	<1,0
8.	A	Rural Diesel Fuel	<6,6	<9,8	<6,6	<10,0
9.	B	Light Diesel Fuel	<2,8	7,4 ± 2,1	<2,8	51,5 ± 12,6
10.	A	Jet Fuel-1	<1,9	<2,0	<3,6	<1,0
11.	C	Jet Fuel-2	<1,0	<1,0	<1,0	<1,0
12.	C	Gasolin-1	<1,0	<1,0	<1,0	28,3 ± 9,8
13.	C	Gasolin-2	<1,0	<1,0	<1,0	<1,0
14.	B	Naphtha	<2,2	6,2 ± 1,0	<4,3	<1,0
15.	C	Heavy Naphtha	<1,0	<1,0	<1,0	<1,0
16.	C	Light Naphtha	<8,0	<10,0	<8,0	<10,0
17.	B	Kerosene-1	<6,9	<9,8	<6,9	<6,8
18.	C	Kerosene-2	7,0 ± 2,6	6,4 ± 2,4	6,0 ± 2,6	62,3 ± 16,9
19.	B	Asphalt-1	<1,0	<1,0	<0,2	<0,8
20.	C	Asphalt-2	<0,7	14,9 ± 3,5	<1,0	<6,8
21.	C	Asphalt-3	<1,2	6,1 ± 2,5	<2,3	68,4 ± 15,5
22.	C	Asphalt-4	1,2	4,4 ± 2,2	<1,2	57,8 ± 7,4
23.	C	Asphalt-5	<1,0	<1,0	<1,0	<1,0
24.	C	Mineral Oil-1	<1,0	<1,0	<1,0	<1,0
25.	C	Mineral Oil-2	<3,6	<5,3	<3,6	<10,0
26.	C	Mineral Oil-3	<1,0	<1,0	<1,0	<1,0
27.	C	Mineral Oil-4	<1,0	<1,0	<1,0	<1,0
28.	C	Mineral Oil-5	<1,0	<1,0	<1,0	<1,0
29.	C	Mineral Oil-6	11,7 ± 4,5	<1,3	11,6 ± 4,5	<14,4
30.	C	Mineral Oil-7	<2,1	<1,1	<2,1	<10,5

The radioactivity concentrations of sludge and scale samples are presented in Table 5. In comparison with the scale samples, sludge wastes have higher activity concentrations. ²²⁶Ra, ⁴⁰K activity concentrations in scale samples are varying from MDA values up to 10.2±1.7 and 52.8±9.0 Bqkg⁻¹ respectively. The activity concentrations of ²²⁴Ra and ²²⁸Ra radionuclides in scale samples were found below of the MDA values.

The activity concentration of ²²⁴Ra, ²²⁶Ra, ²²⁸Ra and ⁴⁰K in sludge samples were measured from MDA values to 343.7±11.8, 809.2±29.0, 302.5±21.6 and 623.0±80.6 Bqkg⁻¹ respectively. Sludge-9 sample has highest activity concentration at all. For the reason that presence of higher activity concentrations in sludge samples radiological parameters were calculated for radiation protection aspect.

Table 5 The activity concentration of ^{224}Ra , ^{226}Ra , ^{228}Ra and ^{40}K in sludge and scale samples

Refinery Code	Sample	Activity Concentration (Bq kg ⁻¹)				
		²²⁴ Ra	²²⁶ Ra	²²⁸ Ra	⁴⁰ K	
1	A	Sludge-1	<10,0	<10,0	<10,0	<10,0
2	A	Sludge-2	<3,9	<6,8	<3,9	<10,0
3	A	Sludge-3	30,2 ± 4,8	263,0 ± 24,7	27,1 ± 9,2	<10,0
4	A	Sludge-4	31,6 ± 4,7	221,5 ± 20,0	58,7 ± 12,0	623,0 ± 80,9
5	A	Sludge-5	<7,0	76,9 ± 8,0	<7,0	<8,0
6	A	Sludge-6	<3,3	227,0 ± 20,0	<3,9	<10,0
7	B	Sludge-7	<1,7	<1,0	<1,7	<6,8
8	B	Sludge-8	<0,6	15,1 ± 1,5	<1,3	<3,8
9	B	Sludge-9	304,3 ± 34,7	809,2 ± 29,0	302,5 ± 21,6	<10,0
10	B	Sludge-10	120,0 ± 15,6	236,0 ± 23,6	110,0 ± 20,9	<10,0
11	C	Sludge-11	<1,0	<1,0	<1,0	<10,0
12	C	Sludge-12	88,8 ± 10,7	159,1 ± 17,0	88,6 ± 17,7	<10,0
13	C	Sludge-13	<1,0	4,3 ± 1,2	<0,8	55,5 ± 9,8
14	B	Sludge-14	343,7 ± 11,8	546,7 ± 25,0	217,4 ± 11,8	202,6 ± 30,4
15	B	Scale-1	<2,0	<5,4	<1,3	<10,0
16	B	Scale-2	<2,8	6,1 ± 1,8	<2,1	<10,0
17	B	Scale-3	<0,5	10,2 ± 1,7	<1,0	52,8 ± 9,0

Radium Equivalent Activity of Sludge Samples

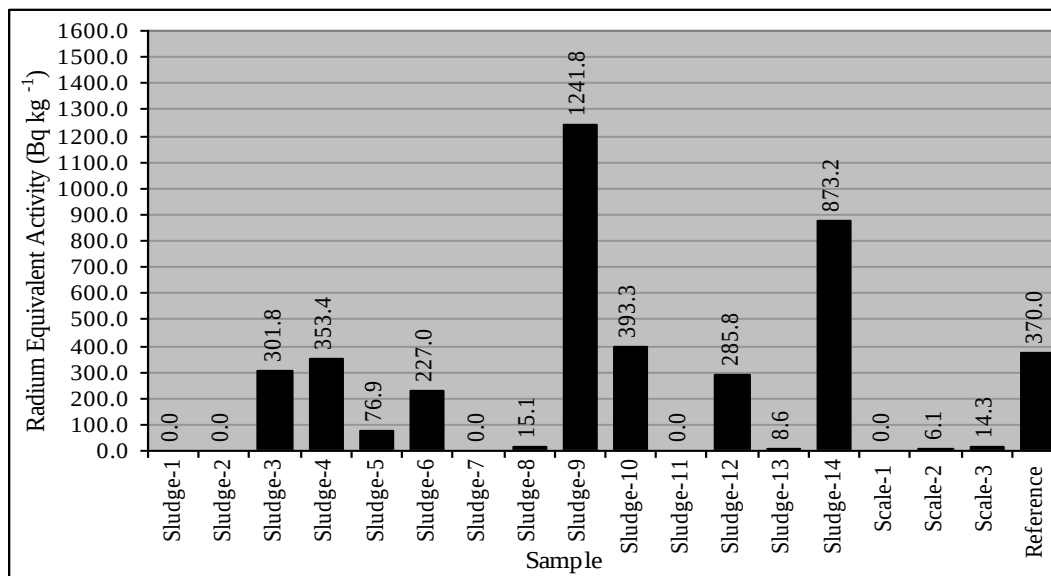
A radiological index for assessment of radioactivity in studied materials is radium equivalent activity (R_{eq}). 370 Bq kg^{-1} and lower radium equivalent activity is regarded as being equal or below of 1.5 mSvy^{-1} external doses for safe use of additive in building materials. Radium equivalent activity connotes

transformation activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K radionuclides into the commonly used index. R_{eq} is calculated given formula [12]:

$$R_{\text{eq}} = A_{\text{Ra}} + (10/7) \cdot A_{\text{Th}} + (10/130) A_{\text{K}} \quad (1)$$

A_{Ra} , A_{Th} and A_{K} stand for specific activities of ^{226}Ra , ^{232}Th and ^{40}K radionuclides in Bq kg^{-1} unit.

Figure 2 Radium Equivalent Activities of Sludge and Scale Samples



^{228}Ra were used instead of ^{232}Th for calculation of radium equivalent activities of sludge samples. Results of calculations are given in Figure 2. 3 residue samples were calculated over the limit value of 370 Bqkg^{-1} . Radium equivalent activities of sludge and scale samples are varying from approximately zero to 1241.8 ± 42.4 value. It is quite obvious that sludge 14, sludge 10 and especially sludge-9 sample has maximum value, are not appropriate to direct use for additive in building materials.

Activity Concentration Index (I_γ) and Alpha Index (I_α)

Activity concentration index or gamma index recommended by European Commission correspond 1 mSv or lower dose if I_γ equal or lower from 1 value. Activity concentration index is calculated by the following formula [13]:

$$I_\gamma = (A_{\text{Ra}}/300) + (A_{\text{Th}}/200) + (A_{\text{K}}/3000) \quad (2)$$

A_{Ra} , A_{Th} and A_{K} are denotes activities of ^{226}Ra , ^{232}Th and ^{40}K radionuclides in Bqkg^{-1} unit. Activity concentration index of residues are given in Figure 3. It is clearly seen in the Figure 3 that 8 sludge samples are higher or equal than the recommended criterion of $I_\gamma \leq 1$. Activity concentration index of sludge-9 sample

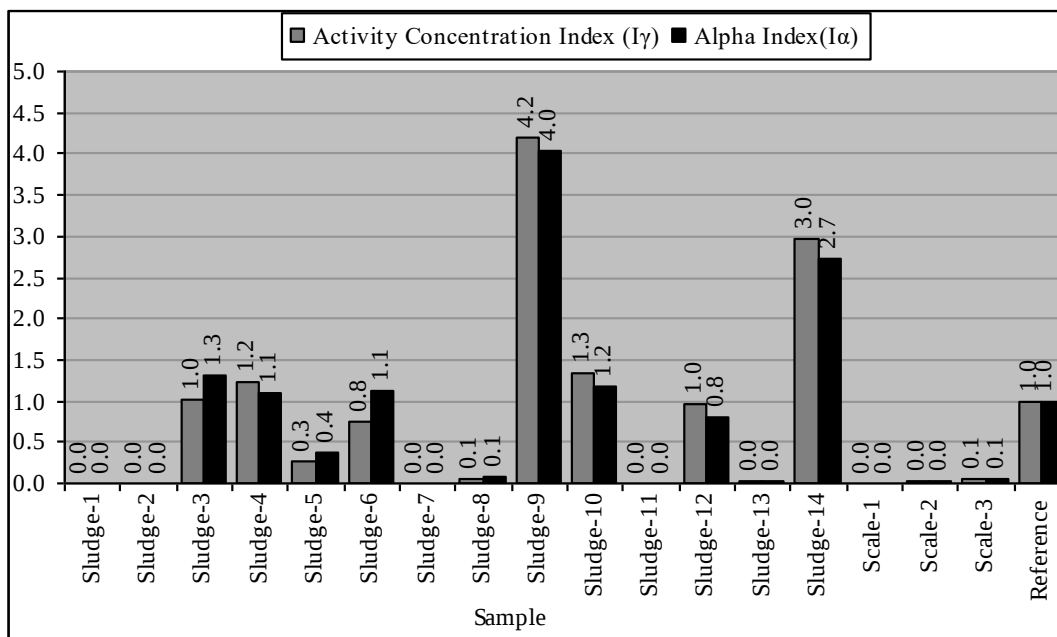
has maximum value is 4.2 times higher than the recommended value i.e. 1 mSv/y .

The two isotopes of Radon gas, ^{222}Rn and ^{220}Rn , decay product of ^{238}U and ^{232}Th series radionuclides are inert and alpha radiation emitter. They can cause internal radiation dose when radon isotopes are taken to the body by inhalation from building materials and working place. Due to the short live time (55. s.) and low level activity, ^{220}Rn is neglected for calculations. ^{222}Rn is the short live significant radionuclide of ^{238}U decay chain and on account of emitting hazardous alpha radiation can cause internal exposure by the time of inhalation. According to the European Commission recommendation ^{222}Rn must be less than 200 and 400 Bq.m^{-3} for new buildings and older buildings respectively. [12]. If I_α is equal or lower from 1, activity concentration of ^{222}Rn in buildings is assessed equal or lower 200 Bq.m^{-3} . Alpha Index is calculated following equation [14]:

$$I_\alpha = A_{\text{Ra}}/200 \text{ Bq.kg}^{-1} \quad (3)$$

A_{Ra} stands for activity concentration of ^{226}Ra radionuclide. As shown in Figure 3, alpha index of sludge and scale samples are ranged from zero to 4.0. Alpha index of 6 residue samples were calculated over the limit value of 1. Sludge sample of Refinery B have considerably high (4 times from reference value) alpha index.

Figure 3 Activity Concentration Index and Alpha Index of Sludge and Scale Samples



Gamma Absorbed Dose Rate and Annual Effective Dose

The absorbed dose rates due to uniform distribution of gamma emitter ^{226}Ra , ^{232}Th and ^{40}K radionuclides 1m

above ground level of sludge residues were calculated from given formula as [15]:

$$D(\text{nGy h}^{-1})=0.462A_{\text{Ra}}+0.621A_{\text{Th}}+0.0417A_{\text{K}} \quad (4)$$

Figure 4 Air Absorbed Gamma Dose Rate (nGy h^{-1})

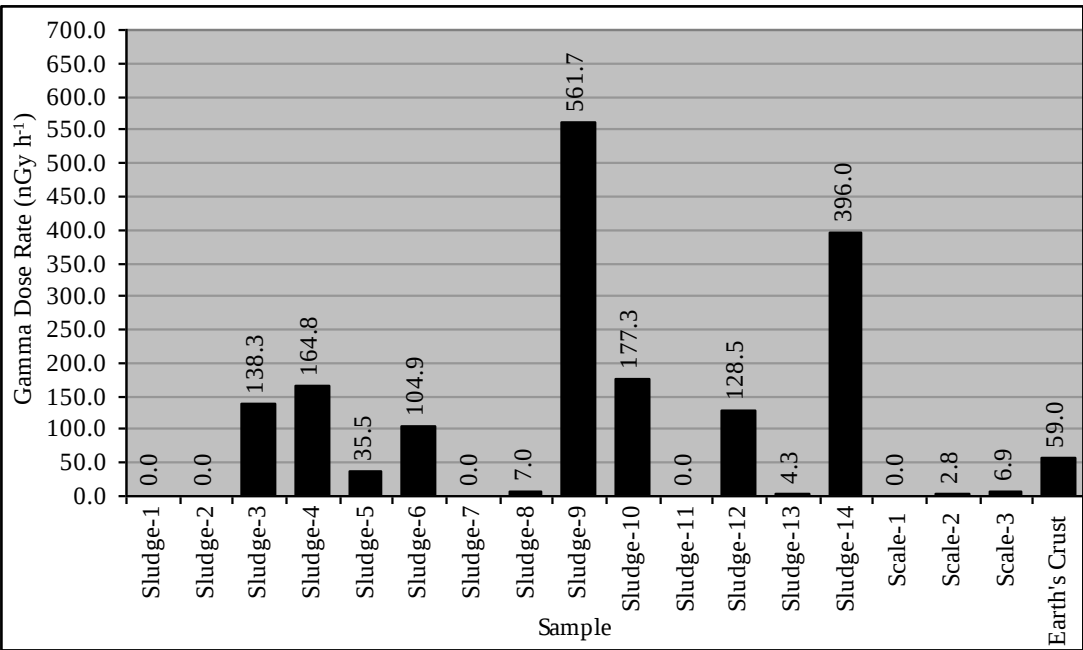
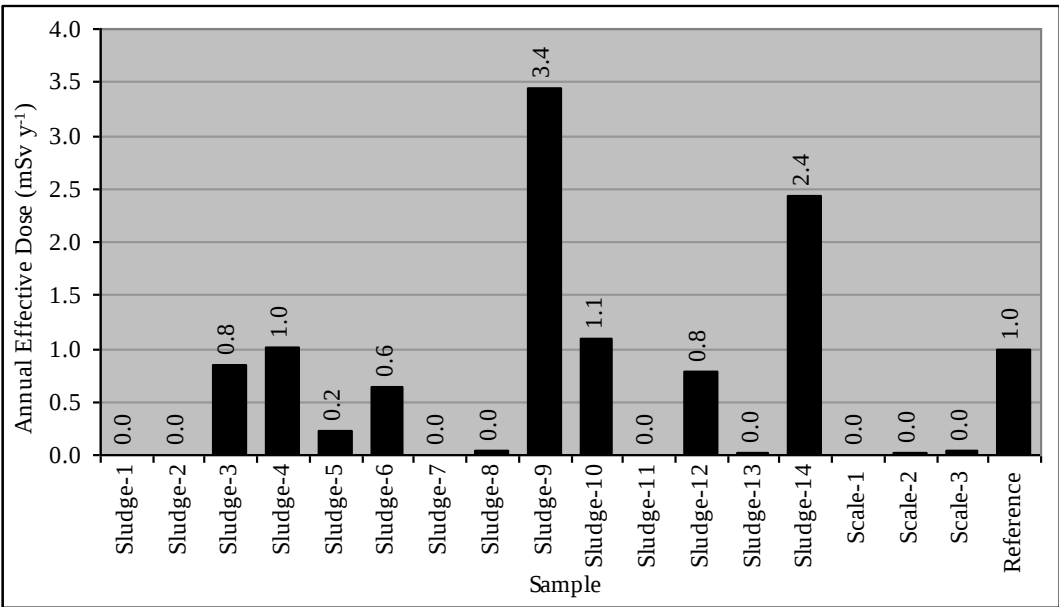


Figure 5 Annual Effective Doses of Sludge and Scale Samples



A_{Ra} , A_{Th} and A_K denote specific activities of ^{226}Ra , ^{232}Th and ^{40}K radionuclides in $Bqkg^{-1}$ unit. Calculation results are given in Figure 4. According to the UNSCEAR 2008 report, average activity concentration of ^{226}Ra , ^{232}Th and ^{40}K radionuclides in earth's crust are 32, 45, 412 $Bqkg^{-1}$ and air-absorbed dose rate of earth's crust is 59 $nGyh^{-1}$ arising from concerned radionuclides. As seen in figure 4, 7 values of dose rates of sludge samples are higher than average earth's crust of 59 $nGyh^{-1}$ that some value of them are reach to a condition of approximately 10 times higher than earth's crust dose rate.

Annual effective dose originated from residues of refinery products are given in Figure 5. Calculations are performed by the following formula [16]:

$$E(mSvy^{-1})=D \times 8760 \times 0.7 \times 10^{-6} \quad (5)$$

D is air-absorbed dose rate in $nGyh^{-1}$. UNSCEAR proposes to multiply by conversion coefficient from absorbed dose in air to effective dose (0.7 $SvGy^{-1}$). Outdoor and indoor occupancy factors were not used in calculations. Reference to the European Commission Reports annual effective dose of adult people must be less than 1 $mSvy^{-1}$. As it is seen in the figure 5, annual effective dose of residue samples are ranged from 0.0 to 3.4 $mSvy^{-1}$.

CONCLUSION

In this investigation total 56 crude oil, refinery product, waste water, sludge and scale samples collected from 3 refineries were measured by gamma spectrometric method for assessment selected radiological parameters. Waste water samples do not contain significant activity concentrations. Measurements results indicated that crude oil and refinery products dose not contain significant activity concentrations and can easily express that they do not pose any danger without calculating radiological parameters. However it is impossible to state same assessment for sludge samples. Activity concentrations of sludge samples were found at elevated levels (up to 809.2 ± 29.0 $Bqkg^{-1}$ for ^{226}Ra) and needed to radiological assessment. Radium equivalent activity of sludge samples were calculated between zeros to 1241.8 ± 42.4 $Bqkg^{-1}$. According to the calculations all sludge samples can't use safely as additive in building materials. For some sludge samples activity concentration index and alpha index were calculated approximately 4 times higher then reference value. Air absorbed gamma dose rate were determined higher from average earth's crust for 7 samples. Sludge-9 was calculated about 10 times higher from average earth's crust gamma dose rate. Annual effective dose arise

from natural radionuclides were found from zeros up to 3.4 $mSvy^{-1}$.

It would appear that due to increasing demand on oil and oil products won't loose their significance foreseeable future. As a consequence of this situation, natural radionuclides accumulations in residues are unavoidable. Even though crude oil and petroleum products do not pose significant danger, sludge samples need to periodically radiological self-checking by continual monitoring program by industrial sectors and also cyclically inspection by regulator body. Especially cleaning or maintenance operations in oil processing facility and during residue dispose operations, naturally occurring radionuclides can cause internal and external exposure of workers also member of the public. From the point of the view of technologically enhanced naturally occurring radionuclides accumulation and additional radiation doses, to protect environment, worker and member of public's health, appropriate precaution must bring into action via radiation protection measures.

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