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Measurement of enhanced radium isotopes in oil production wastes in Turkey

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ABSTRACT

Gamma dose rates of oil production equipment and wastes were measured externally by survey meter. They were found to be between 0.2 μSv h^{-1} and 25.7 μSv h^{-1}. Activity concentrations of radium isotopes in crude oil, scale, sludge, contaminated soil and water samples were determined by gamma spectrometric method. Activity concentrations of ^{224}Ra, ^{226}Ra and ^{228}Ra in samples varied from MDA to 132,000 Bq kg^{-1}. Radium isotopes enriched up to 14,667 times in scale samples. The highest value of ^{226}Ra was found to be 35,122 ± 1,983 Bq kg^{-1} for sludge samples. Activity concentrations of a considerable number of samples were found to be higher than the exemption level recommended by IAEA. Measurement results revealed that oil production wastes caused soil contamination up to 70,483 Bq kg^{-1}. They may pose a radiological risk for workers and members of the public.

1. Introduction

The presence of naturally occurring radioactive materials (NORM) in oil and gas industry has been known since the beginning of 1900s (IAEA, 2003; Mc Lennan, 1904). Many studies have been reported for scale and sludge wastes originated from oil and gas industrial processes (API, 1992; Al-Masri et al., 1997). In these studies, ^{226}Ra activity concentrations have been found well above natural background levels. Moreover, the activity concentration of ^{226}Ra has been found to be 15 M Bq kg^{-1} in a published scientific study (Jonkers et al., 1997).

The production quantities and radionuclide concentrations of NORMs depend on many parameters in particular geological structure of reservoir. Activity concentrations of NORMs may incompatible with each other even if samples are taken from different wells of same region. Therefore, each study contains original results concerning NORM information in oil industry.

Petroleum maintains its importance as one of the most prevalent energy sources in the today's world due to the continuous increase of its demand and production. Therefore, possible detrimental effects of petroleum origin NORM wastes to workers or members of public also keep its significance as a common radiological concern even today. Many institutions and researchers still work on the NORM problems in oil industry for this reason (Bassioni et al., 2012; Khodashenas et al., 2012).

^{238}U, ^{235}U and ^{232}Th decay series, ^{87}Rb and ^{40}K are known as primordial naturally occurring radionuclides. They are found on more or less in every material from Earth's crust or industrial wastes (IAEA, 2010). ^{226}Ra from ^{238}U series, ^{224}Ra and ^{228}Ra from ^{232}Th series and ^{40}K are frequently encountered radiologically significant radionuclides in oil and gas industry. Therefore, researchers mostly regard these radionuclides as significant in their studies.

Crude oil, formation water, and gas are found as a mixture in reservoir. The formation water contains many cations of calcium, strontium, barium, radium and their isotopes (IAEA, 2010). These isotopes are found as dissolved in the water and occurred in consequence of water–rocks interactions. When the liquid mixture reach to the surface, radionuclides can accumulate on the inner part of equipment as scale due to changed thermodynamic conditions (such as temperature, solubility, pressure, acidity etc.). Scale is a compound of sulphate and/or carbonate (Parmaksız et al., 2013).

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^{238}U and ^{232}Th, which are parent radionuclides of natural radioactive series, have a low solubility in water. Therefore, they do not reach to the surface from reservoir through the oil-gas-water mixture. However, their decay product radionuclides (^{226}Ra, ^{224}Ra and ^{228}Ra) migrate to the surface through the oil-gas-water mixture. Thus, ^{226}Ra, ^{224}Ra, and ^{228}Ra are regarded as "unsupported radionuclides" in the oil and gas industry (Shawky et al., 2001). Many researchers have paid special attention about scale, sludge or produced water containing elevated activity concentrations in the oil industry (Parmaksız et al., 2013; Bakr, 2010; Darko et al., 2012).

There is not a comprehensive study concerning NORMs generated from oil production industry in Turkey. However, it was known that high dose rates were detected from outer surface of some equipment of oil wells and their scrap metals generated in maintenance operations of oil production facilities. A recent study concerning sludge wastes gave an important hint about the possibility of having NORMs with high activity concentrations in oil production facilities in Turkey (Parmaksız et al., 2013). In the aforementioned study, enrichments of naturally occurring radionuclides were determined in residues of oil refineries.

According to the Environmental Protection Agency (EPA), petroleum industry generates approximately 260,000 metric tons NORM waste (produced water, scale, sludge, and contaminated equipment) in every year in the United States (EPA, 2013). The United States and Turkey produce 325.2 and 2.4 million tons of oil per year respectively (PIGM, 2013). Considering these data, it is estimated that the oil industry have produced approximately 19,000 metric tons of NORM waste in the last decade in Turkey.

Gamma dose rates of well components (scrap metals, production manifolds, separators, production lines etc.) were directly measured from the outer surface of the equipment by dose rate meters in this study. Activity concentrations of ^{224}Ra, ^{226}Ra and ^{228}Ra radionuclides in water, contaminated soil, scale, and sludge samples collected from oil production facilities were determined by using gamma-ray spectrometers and finally results were discussed.

2. Material and method

2.1. Study area

The study area is located in the southeast part of Turkey (Fig. 1). The oil production is carried out in 26 different oil fields by using 209 oil wells in the region. In the country, approximately twenty percent of petroleum production is carried out in this region (Silkroad development agency, 2014). Four hundred cubic meters of natural gas are also produced per day in the region. It corresponds approximately one percent of natural gas production of the country.

Scale, which occurs in consequence of maintenance operations of equipment, is deposited in waste storage area. Many scrap metal equipment (production lines, pumps etc) contaminated by NORM are also deposited in the storage area. Sludge that is formed during oil production processes are deposited in warehouse and a portion of them is embedded in the ground without any radiation protection measures. Water, which rises to the surface by oil-gas-water mixture, or originates from production processes, is injected back into wells so as to enable pressure balance.

2.2. Dose rate measurements

There are many methods for measuring radiation. The most practical and widely used method among these is to measure of radiation dose rate by survey meter. It is very useful and convenient method for detecting radiation as initial examination tool. Therefore, dose rate measurements were performed primarily for the detection of radiation in this study. Commercially available Radiagem 2000 personal portable dose rate and survey meter was used for measurements. Ambient dose rates were measured initially in order to eliminate contributions of terrestrial and cosmic radiation. Then, they were subtracted from dose rates of studied samples.

Radiagem 2000 personal portable dose rate and survey meter, which has a Geiger Mueller energy compensated detector, is suitable for gamma and X-ray measurements. It has a measurement range between 0.01 μSv h^{-1} and 100 mSv h^{-1}. Radiagem 2000 personal portable dose rate and survey meter has an energy range (International electrotechnical commission-IEC 60846) from 40 keV to 1.5 MeV. It has also a sensitivity of 0.83 c/s per μSv h^{-1}, an accuracy of ±15%, a response time range of 1 s–10 s for average. Radiagem 2000 personal portable dose rate and survey meter has features of complete and automatic self-test when switching on and periodical control of main function when in use.

Radiagem 2000 personal portable dose rate and survey meter is calibrated periodically by the Secondary Standard Dosimeter Laboratory (SSDL) of the Çekmece Nuclear Research and Training Center (ÇNAEM). SSDL is a member of IAEA/WHO Network of SSDLs and continues its activities in Metrology Department of ÇNAEM of the Turkish Atomic Energy Authority (TAEK).

2.3. Sampling and sample preparation

Fifty-four samples (crude oil, water, scale, sludge and contaminated soil) were collected from the oilfield processing units and waste disposal sites. Crude oil and water samples were taken from processing units and separators. Scale samples were collected from waste sites, storage tanks, their scrap equipment generated in maintenance operations, and their residues accumulated on the inner surface of pipelines (Fig. 2). Sludge samples were taken from barrels stored in processing units and final disposal sites (Fig. 3).

Determination of activity concentration of radionuclides in soil is not an object of this study. However, sludge has poured around some wells and cause soil contamination. Sludge transforms into liquid phase from solid phase at temperature over 35°. In the studied region, temperature mostly rises above 40° in the daytime of summer. Maintenance operations of wells were performed a long time ago and sampling time coincided with the summer. Therefore, pure sludge samples could not be taken for some wells. Soil samples contaminated by sludge during maintenance operations were collected instead of sludge from around the wells. Soil samples were taken from 4 to 5 cm of surface soil because contamination (leakage) was not observed beyond the 4–5 cm surface soil.

Samples were put into 1 L plastic container, labelled, arranged as motionlessly transport and brought to Health Physics Department of the Sarayköy Nuclear Research and Training Center. Two different sample preparation procedures were applied for samples in internal dosimetry laboratory.

Routine sample preparation procedure was applied for scale and contaminated soil samples. Initially, they were heated in a temperature controlled drying oven at 105 °C until their moisture was completely removed. Then, samples were filled into cylindrical plastic analysis containers, which have 6 cm diameter and 5 cm height. They were weighed, hermetically sealed with parafilm and kept for at least 30 days to reach secular equilibrium between ^{226}Ra and its short half-life daughters (^{214}Pb and ^{214}Bi).

For sludge, routine sample preparation procedures could not be applied properly because it was observed that sludge samples transform into the liquid phase from solid phase at temperature over 35°. Plastic analysis container could not be used for measurements due to containing a small amount of organic impurities.