TA6 Radiation Protection of the Public and the Environment

RADIOLOGICAL IMPACT OF OIL/GAS INDUSTRY

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INTRODUCTION

The mining, milling and industrial use of naturally occurring radioactive materials (NORM) covers a range of mineral resources and industrial activities. The main so non-nuclear industries include phosphoric acid and fertilizer production; iron and steel production; coal and gas fired power plants; coal tar processing; extraction of coal, oil and gas; building materials industry; mineral sand; titanium pigment production, and uranium and thorium mining [1,2,3]. There are no radiological controls on the operation of these industries or restrictions on how waste is discharged (to the atmosphere, to landfill or being sold) which relate to its radionuclide content.
Radionuclides are known to be associated with organic materials in nature. Therefore, oil, gas and oil field brines frequently contain radioactive materials [4]. These materials accumulate in piping used to remove and process petroleum and natural gas.
Radioactivity in oil and gas production and processing equipment is of natural origin [5,6,7]. Naturally occurring radioactive elements such as uranium, radium, and radon are dissolved in very low concentrations during normal reactions between water and rock or soil. Ground water that coexists with deposits of oil can have unusually high concentrations of dissolved constituents that build up during prolonged periods of water/rock contact. Uranium and thorium compounds are mostly insoluble, therefore remain in the underground reservoir and as oil and gas are brought to the surface. Many oil-field brines are particularly rich in chloride, enhancing the solubility of other elements including the radioactive element radium. Radium concentrations tend to be higher in more saline water [8]. Some of this saline, radium-bearing water is also extracted with the oil and gas. Some radium and radium daughter compounds are slightly soluble in water and may become mobilized when this production water is brought to the surface.
Since in the Eastern Romania there are two oil and gas regions in Bacău and Brăila districts, which represent about 25% from Romanian oil-field exploitation (over 10,000 wells) we aimed to the assessment of radium-226 content of oil-field waters and possible pollution of these zones with this radionuclide.
The objective of this study was to assess the radiological impact on the environment and population of the oil/gas industry that is non-nuclear industry but uses and can produce materials, with an enhanced content of naturally occurring radionuclides.

MATERIAL AND METHODS

1200 samples of formation water arising from oil wells, water injection wells and treating stations were drawn and analysed for their radium-226 content.

The oil and gas production may produce radioactive pipe scale (a residue left in pipes from drilling oil wells) and sludge (that leaves sites and equipment contaminated); therefore we sampled scale and sludge (75 samples).

Extensive measurements of the levels of natural radioactivity in environmental samples in the selected areas were performed. The main radionuclides investigated in the uranium series were uranium-238, polonium-210, radium-226 and in the thorium series we looked at thorium-232. In addition, potassium-40 was determined.

High-resolution gamma spectrometry, alpha spectrometry techniques and radiochemical and physical methods carried out in conformity with the current national standards and settlements were applied.

Active measurements of gamma ray dose rate were carried out using Inspector Nuclear Radiation Monitor (MEDCOM) – SUA (autoscale of 0.01 μSv/h – 1 mSv/h).

Soil (280 samples), vegetation (90 samples) and 120 samples of ground and surface water have been collected from those two major petroleum-producing regions. The soil (top 5 cm and 5-15 cm) and vegetation samples were collected from 400 sq. cm surface.

All the solid samples (soil, scape and sludge) were dried at 105^0C and after grinding were passed through 12-mesh sieve. The sieved samples were placed in the plastic Marinelli beaker and stored for 30 days to allow build up and reach radioactive equilibrium of radon and its daughters. After this period those samples were measured. Measurements were performed on characteristic samples obtained from ten individual homogenized samples.

The vegetation samples were dried, calcined and wet mineralized. Arising acid extracts were utilized for the assay of natural radioelements like in water.

The method used for the determination of the radium-226 content in water collects the radon-222 gas product of the decay of radium-226. Its radioactivity is measured by alpha rays measurement in a scintillating chamber and extrapolated back to the concentration of radium-226. The combined standard uncertainty varied in the range 0.01-0.11 Bq/L and the limit of detection was of 0,003 Bq/L. Uranium-238 and thorium-232 were calculated after determining the content of natural uranium and thorium by the method based on their separation and purification on a strong basic anion exchange resin and spectrophotometric measurements in the form of their Arsenazo III complex. The assay of polonium-210 was done by electrochemical deposition and alpha counting of polonium-210 deposited on the nickel disc in a low background ZnS (Ag) scintillation counter. The assay of lead-210 was done by electrochemical deposition (65% radiochemical recovery) and beta counting of lead-210 deposited on the nickel disk using counting equipment with anticoincidence counter (20% efficiency). Potassium-40 was found by calculation after the photometry dosing in flame emission mixture of potassium natural isotopes.

RESULTS AND DISCUSSION

The formation water must be separated and then disposed, usually by return to depth in an injection well. The present NORM in oil and gas production streams occasionally accumulates as scale or sludge in tubing and surface equipment. NORM radioactivity levels in produced water, scale and sludge usually are characterized in terms of radium activity level (Radium-226 and Radium-228).
Because the activity level of ^{226}Ra usually is three times that of ^{228}Ra, Radium-226 is the primary isotope of concern with respect to long term radiological concerns in environmental impact [6, 8].
Radium-226 concentrations from 0.005 Bq/L up to more 10 Bq/L were found in the formation water samples arising from oil wells, water injection wells and treating stations (table 1).
One should remark that 90% of samples exceeded by far the specific activity of surface water, excepting the Oprisenesti zone. We must give this problem our careful consideration taking into account that these formation waters are not reinjected in all situations, being accidentally discharged into watercourses and into cultivated or meadow lands.

Table 1. Activity concentration of ^{226} Ra in water samples originating from oil areas

DISTRICT	OIL FIELD	Water type	Radium-226 (Bq/L) Range	Average ± SD
BACĂU	MOINESTI	Formation water	0.07 – 10.24	3. 72 ± 1.99
	MODARZAU	Formation water	0.17 – 4.45	2.53 ± 1.62
	ZEMES	Formation water	0.15 – 4.39	1.72 ± 1.53
	MOINESTI, ZEMES, MODARZAU	Ground and surface water	0.003 – 0.199	0.053 ± 0.039
BRĂILA	BORDEI VERDE	Formation water	0.052 – 0.077	0,067 ± 0,008
	OPRISENESTI	Formation water	0.005 – 0.019	0,009 ± 0.005
	IANCA	Formation water	0.034 – 5.05	1.70 ± 2.05
	BORDEI VERDE, OPRISENESTI, IANCA	Ground and surface water	0.007 – 0.127	0.044 ± 0.032

The radium-226 concentrations of the ground and surface water in the same territory varied in the range 0.003-0.199 Bq/L. These values were much smaller than that in oil-fields water, for the time being.

At oil-field sites the pipes and tanks that handle large volumes of this "produced water" can become coated with scale deposits that contain radium. Radium-bearing scale is the type of "diffuse NORM waste" that commonly occurs in the oil industry [7, 9-12]. When radium substitutes into the barium sulfate or calcium carbonate scale, it causes the scale to become radioactive. Once formed, the barium sulfate scale is nearly impossible to dissolve. Mineral deposits in the form of radioactive scale and sludge can be progressively formed in production tubular and surface processing and transportation equipment. Since the radium concentrations in the original formation are highly variable, the concentrations that precipitate out in sludge and as scale on internal surface of oil and gas production and processing equipment are also variable. The scale is relatively insoluble and may vary in thickness from a few millimeters to more than 2 cm. NORM-contaminated scales and sludge is found in production equipment, such as wellheads, heaters treaties, and storage tanks, as well as the pipe connecting the equipment.

We found the highest concentrations of radium reaching up to ten thousand of Bq/kg in scale deposited in wellhead piping and in production tubing near wellhead. There was a decrease up to one order of magnitude of this concentration of radium deposited in separators (870 Bq/kg), the lowest value being found in heaters/treaties (280 Bq/kg).

Some of the solids in the original product stream are removed in the separator, the treatment equipment and tanks and accumulate there as sludge. Radium-226 concentrations in sludge were much lower than concentrations in pipe scale (table 2).

Table 2. Activity concentration of ^{226}Ra in scale and sludge samples

Type of sample	Radium-226 (Bq/kg) Range	Average
SCALE	287 – 9260	3200 ± 1310
SLUDGE	21 – 330	120 ± 67

Radium-226 dominates sludge and pipes scale accumulations, while deposits on interior surfaces of gas plant equipment are predominantly Lead-210 with its decay product Polonium-210, up to 3060 Bq/kg. Therefore, all the oil field equipment must be surveyed for the presence of enhanced natural radioactivity.

The only way to remove the scale is to drill it out or otherwise physically remove it. Some scale is removed at the well site during work over operations. As a result, NORM contamination was found on the ground where work over operations have been conducted to remove scale, either at the well site or at a remote pipe-cleaning yard. Most scale is recovered from equipment when this is sent to a facility for cleaning. More external gamma exposure and dust inhalation occurs for workers when contaminated scale or sludge is cleaned from the inside surfaces of equipment during well work over operations [10].

Measurements in soil and vegetation had clearly shown somewhat higher local activity values for radium-226 content related to accidental discharges of oil-field brines. Local activities up to about 330 Bq/kg of soil and the relatively higher external dose rates up to 400 nGy/h, (two times natural radiation background) were associated with these areas around formation water discharge and handling system and descaling of pipes.
The activity concentration values in soil, surface water and spontaneous vegetation originated in oil field areas are reported in table 3 comparatively with usual values for Romania.

Table 3. Typically encountered activity concentration of natural radionuclides associated with oil and gas industry

Component of Environment	Industry	Activity mass concentration (range)			
		^{238}U	^{226}Ra	^{232}Th	^{40}K
Soil Bq/kg	Oil/gas-field Usual values	2.4 – 120 8 – 60	60 – 330 8 – 72	8 – 87 11 – 75	53 - 960 250 - 1100
Surface water mBq/L	Oil/gas-field Usual values	0.043 – 1.1 0.35 – 18.5	23 – 45 1.8 – 22.5	0.2 – 8.0 1.5 – 12.2	221 - 899 25 - 670
Spontaneous vegetation Bq/kg	Oil/gas-field Usual values	0.2 - 55 0.7 - 48	3.7 – 62 1.8 – 18.7	0.05 – 0.12 1.6 – 3.5	710 - 1100 350 - 640

- The concentrations of uranium, thorium and potassium in the upper 5 cm layer of soil were generally higher in the surroundings of the investigated oil fields and wells but were comparable to the representative values for the Romania [13, 14].
The average value of annual absorbed dose rate in air from terrestrial gamma radiation (mGy/y) related to this non-nuclear industry is of 0.61, smaller than those related to the other non-nuclear industries (0.72 for Coal Fired Power Plants and 0.64 for Phosphate Fertilizer Plant) [15]. These values, even higher, are comparable with the annual average absorbed dose rate in air from terrestrial gamma radiation in Romania that is of 0.52 mGy/y [16].
- The natural radioactivity levels for thorium-232 and potassium-40 detected in surface water are generally comparable to those found in the other zones of Romania. The values of radium-226 are little higher than the corresponding concentrations found generally in Romanian surface waters [13-16]. One should remark that the values for neither of the analysed groups of samples exceeded the level for specific admitted activity in Romania

even for fresh water, for any of the natural radioelements under investigation.

- The vegetation samples showed somewhat higher local activity values for radium-226 content of up to 62 Bq/kg, related to accidental discharges of formation water areas being much higher than that determined in other areas [14].

CONCLUSIONS

- *The natural radioactivity levels in the oil field environmental media, which could represent a risk for the people living in the areas influenced by this non-nuclear industry, do not indicate an increase in the natural radiation background.*
- *From a radiological point of view, the situation does not pose any immediate concern. Some places however need further investigations, with special emphasis on the control of ^{226}Ra releases to prevent from polluting the environment with this radionuclide.*
- *The growing concern amongst the population about the quality of their environment increases the significance of impact assessment of radioactive releases into the environment even if natural radionuclides occur.*

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