

Radium-226 and Radium-228 in Scale and Sludge Generated in the Petroleum Industry

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Abstract. Technologically enhanced naturally occurring radioactive material (TENORM) can accumulate at elevated concentrations in by-product waste as a result of oil and gas exploration and production activities (E&P). The sources of this contamination are the radionuclides from the ²³⁸U and ²³²Th series, which are present in the geological formations that contain oil, gas and water. When water is brought to the surface along with oil and gas, radium, which is dissolved in the produced water, co-precipitates with barium, strontium, or calcium sulfates thus forming scale and sludge. The main radionuclides of concern from the radiological point of view are ²²⁶Ra and ²²⁸Ra. Scales and sludge can contain high quantities of radium and other decay products that can cause exposure of maintenance and other personnel to hazardous radionuclides concentrations. This work presents the results of measurements of the radionuclide content of both scale and sludge samples taken from PETROBRAS units in the State of Sergipe, in Northeastern Brazil. Samples were collected directly from the inner surface of water pipes or from containers stored in the waste storage area of the maintenance unit. The radionuclide contents of scales and sludge were determined through gamma spectrometry analysis by using an HPGe gamma spectrometric system (CanberraTM). Values as high as 1,399.1 kBq·kg⁻¹ for ²²⁶Ra and 742.6 kBq·kg⁻¹ for ²²⁸Ra were determined for sludge samples taken from two different containers. One of the scale samples, taken from the inner surface of a produced water pipeline, had radium concentrations of 629.7 kBq·kg⁻¹ for ²²⁶Ra and 403.1 kBq·kg⁻¹ for ²²⁸Ra. The results indicate that special care must be taken during cleaning operations in order to reduce the exposure to maintenance personnel as well as to avoid contamination of the environment.

Key words: petroleum, sludge, scale, radium, TENORM.

1. Introduction

Technologically Enhanced Naturally Occurring Radioactive Material (TENORM) is formed when naturally occurring radioactive material (NORM) concentrates after industrial processes. Several industries are capable of concentrating NORM at their installations either in their waste by-products or in a product itself. TENORM wastes often come from industrial activities such as thorium and uranium mining/milling; gold, niobium or tin mining; water treatment; phosphate fertilizer; coal fire ash; aluminium production and, last but not least, from oil and natural gas production. The scientific community has been concerned for some time with the risks coming from exposures to these materials. The potential threat posed by these wastes must be investigated [1].

TENORM wastes are generated in the petroleum industry in the form of scales, sludge and produced water. Scales are formed in the interior surface of ducts, pumps, and valves and also on the walls of separation and storage tanks. Sludge is a mixture of residues left in the process. It is made up of the sand pumped up during extraction of the oil, heavy hydrocarbons like paraffin and pieces of scale detached from the walls. The other type of waste is produced water, which comes out with the oil. Produced water is a combination of the formation water, which occurs naturally in the reservoir, and the water injected in the well to increase the pressure necessary for extracting the oil [2].

Formation water may be rich in chloride or sulphate salts and alkaline earths such as calcium, barium, radium and strontium that dissolve from the rocks that surround the reservoir. The water injected in the wells can come from nearby water wells, but most of the time the produced water is re-injected back into the process. When these two types of water are brought together, the chemical equilibrium is disrupted and salt precipitation may occur. This is even more intense when the mixture oil/water is

pumped up and differences in temperature, pressure and flow velocity occur, resulting in the formation of BaSO₄, SrSO₄, CaSO₄ and CaCO₃. These precipitates will concentrate and accumulate in different parts of the process, forming scales and sludge [3-5].

The formation of these residues can impair the oil extraction process. It reduces the area for the flow and can even plug the ducts, causing considerable production losses. Expensive cleaning procedures can be involved once formation of these residues occurs [6]. Removing the scales is a common practice in the oil industry. It can be done either by mechanical means or by the addition of chemicals [7-8]. For the soft carbonate scales, mechanical abrasion should be effective to remove it. On the other hand, the barite scales are hard and insoluble in aqueous solutions and special chemical products are necessary to remove them. The scale removers are based on ethylenediaminetetraacetic acid, which acts producing water-soluble complexes, thus preventing the cations from reacting with available anions and precipitating. The use of scale inhibitors or scale removers is not as cost effective as the physical removal of scales [9].

Radium may be included among the cations leached from the rocks into the formation water. In contrast with radium, only trace amounts of ²³⁸U, ²³²Th, ²²⁸Th, ²¹⁰Pb, ²¹⁰Po and other radionuclides enter the brines due to the low solubility of these elements [10]. When produced waters are brought to the surface along with the oil, these radionuclides, especially radium, come along with it. Due to the chemical similarity of radium with calcium, strontium and barium, it coprecipitates with these elements during scale formation. The main radioactive element in scale and sludge is radium. Its presence has been recorded in several occasions [9,11]. ²²⁶Ra, from the ²³⁸U series and its daughters ²¹⁰Pb and ²¹⁰Po together with ²²⁸Ra and ²²⁸Th from the ²³²Th series are the dominant isotopes [12-13]. Concentration values of some of these elements in scales, sludge and produced water are reported in Table I.

Table I. ²²⁶Ra and ²²⁸Ra activity concentration for scale and sludge samples collected from different studies.

Reference	Country/ material	²²⁶ Ra kBq·kg ⁻¹	²²⁸ Ra kBq·kg ⁻¹	²²⁸ Th kBq·kg ⁻¹	²¹⁰ Pb kBq·kg ⁻¹
[14]	Brazil/scale	19.1 to 323.0	4.21 to 235.0	-	-
[14]	Brazil/sludge	0.36 to 367.0	0.25 to 343.0	-	-
[15]	Algeria/Hard scale	1.0 to 950.0	-	-	-
[15]	Algeria/Soft scale	1.0 to 300	-	-	-
[16]	Tunisia/ scale	4.3 to 658	-	-	-
[16]	Algeria/sludge	0.069 to 0.393	-	-	-
[17]	Norway/ scale	0.3 to 32.3	0.3 to 33.5	-	-
[17]	Norway/sludge	0.1 to 4.7	0.1 to 4.6	-	-
[18]	Brazil/scale	< 839	< 377	-	-
[18]	Brazil/sludge	3,060	2,570	-	-
[19]	Various locations	< 1,000	< 360	< 360	< 72

The protection of the workers is of special concern when dealing with TENORM in the oil industry. The two primary routes of exposure are inhalation of dusts and external exposure to gamma radiation from bulk storage of the material. Dose from ingestion of radioactive material is not considered to be significant. The main routes of exposure are inhalation of dusts during equipment cleaning and exposure to gamma radiation close to pipelines and vessels, which concentrate radionuclides [20]. ²²⁶Ra, an alpha emitter, is a potential internal hazard to workers from the inhalation of the dust produced during pipe cleaning operations. Due to the lower abundance and short half-life, ²²⁸Ra is not as important as ²²⁶Ra [11].

2. Material and methods

Twenty-two samples were collected from PETROBRAS E&P units in the state of Sergipe/Brazil. Gamma surveys were done around pipelines and equipment at various locations in order to identify the points in the process where gamma radiation was high enough to cause risks to the workers. The same was done around the barrels in the storage area located in the patio of the maintenance unit. These barrels are filled with scale and sludge that were removed from tanks and ducts during cleaning and maintenance operations. The survey was done with an Ionization Chamber Survey Meter model 450 from VICTOREENTM.

Sludge samples were taken either from inside the barrels stored in the storage area or from the bottom of equipment that had been opened for cleaning and maintenance. Scales were collected from the inside walls of ducts and equipment and from barrels stored in the patio. Two samples were taken from a production-holding pit close to the E&P area. This pit was used in the past for increasing separation of oil, water, and sediment. The sediment remaining in the pit is composed of an oily, viscous material called sludge. Table II describes all the samples and shows the place where they were collected. Samples 16 to 22, excluding sample 18, were collected from secondary manifolds (which receive oil from a small number of wells) Sample 18 was collected from the main manifold, at the entrance of the collecting and processing station, where the oil is separated from the water and gas.

Table II. Samples description and location.

Sample number	Sample type	Origin
1	Sludge	Barrel
2	Sludge	Barrel
3	Scale	Produced water pipeline
4	Sludge	Barrel
5	Sludge	Barrel
6	Sludge	Barrel
7	Scale	Produced water pipeline
8	Scale	Produced water pipeline
9	Sludge	Holding pit
10	Sludge	Holding pit
11	Scale	Produced water pipeline
12	Sludge	Barrel
13	Sludge	Barrel
14	Sludge	Barrel
15	Sludge	Barrel
16	Scale	Secondary manifold / oil pipeline coming from wells
17	Scale	Secondary manifold / oil pipeline coming from wells
18	Scale	Main manifold / oil pipeline coming from wells
19	Scale	Secondary manifold / oil pipeline coming from wells
20	Scale	Secondary manifold / oil pipeline coming from wells
21	Scale	Secondary manifold / oil pipeline coming from wells
22	Scale	Secondary manifold / oil pipeline coming from wells

After collection, the samples were taken to the laboratory, to be measured. The samples were placed in 5 cm diameter and 1 cm height cans, weighted and sealed with both silicone and black electrical tape. They were left undisturbed for one month, the time necessary for the ingrowth of the progeny from both ^{238}U and ^{232}Th series. After that time, their radionuclide content was determined through gamma-ray spectrometry.

The concentrations of ^{226}Ra and ^{228}Ra in the samples were determined by using a high purity germanium detector (HPGe) from CanberraTM with Canberra Genie PC software. In order to reduce the influence from background counts on the results, the detector was involved in a low background lead shield. Counting time was at least 10,000 seconds, in order to accumulate enough counts under the peak and keep down the errors in the measurements. Due to the high activity of some samples and to avoid the sum peak effect an 11 cm distance between sample and detector was used. In some cases, when the activity was even higher, a 19 cm distance needed to be used.

Calibration of the system was carried out through different single-element radioactive sources, including ^{133}Ba , Cd-109, Cs-137, Co-57, Co-60, Na-22, and Mn-54. They were first used for energy calibration of the equipment and also for the determination of the efficiency. The efficiency was calculated for both geometries, by counting the point sources at 11 and 19 cm distance from the detector.

Both ^{226}Ra and ^{228}Ra were measured taking into account the condition of secular radioactive equilibrium between ^{226}Ra , ^{228}Ra and their direct progeny. Concentration values for ^{226}Ra were calculated by measuring the total counts under the 609.3 keV peak of ^{214}Bi . This higher energy peak was chosen instead of the 352 keV peak of ^{214}Pb to avoid problems with the auto-absorption of the lower energy gamma rays. The 186.2 keV line emitted by ^{226}Ra was not used in these measurements because it is too close to the 185.7 keV line from ^{235}U and the uncertainty in the measurement can be high.

The concentration values for ^{228}Ra were obtained by integrating all the counts under the peak for the 911 keV gamma ray of the ^{228}Ac , one of its progeny. ^{228}Ra does not emit any gamma ray of significant energy to be able to be measured directly, especially for low concentrations in the sample.

The activity concentration (A) for each of the radionuclides was then determined through the equation:

$$A = \frac{C}{\varepsilon \cdot y \cdot m} \quad (1)$$

where C is the full-energy peak count rate of the measured radionuclide (in counts per second), ε is the efficiency of detection for the specific energy, y is the yield of the gamma-ray under consideration, and m is the mass of the sample, expressed in grams.

3. Results and discussion

Dose rates as high as $140 \mu\text{Sv}\cdot\text{h}^{-1}$ were measured on the surface of water pipelines, mainly close to valves or elbows, where solid particles tend to accumulate. In the storage area, on the other hand, dose rates of up to $700 \mu\text{Sv}\cdot\text{h}^{-1}$ were measured on the external surface of some barrels. These values are extremely high if we consider that the maximum limit for exposure rates for the majority of the states in the United States is $50 \mu\text{Sv}\cdot\text{h}^{-1}$ for equipment contaminated with NORM [21].

Concentration values for both ^{226}Ra and ^{228}Ra can be found on Table III, for all the twenty-two scales and sludge samples collected from barrels, from the inner surface of produced water pipelines and from ducts coming from the oil wells, as described on Table II.

Table III. ^{226}Ra and ^{228}Ra activity concentrations for scale and sludge samples.

Sample number	Sample type	^{226}Ra ($\text{kBq}\cdot\text{kg}^{-1}$)	^{228}Ra ($\text{kBq}\cdot\text{kg}^{-1}$)
1	Sludge	1399.1	742.6
2	Sludge	57.6	40.0
3	Scale	76.8	92.6
4	Sludge	60.6	42.8
5	Sludge	63.8	43.6
6	Sludge	1,272.6	677.7
7	Scale	78.9	69.5
8	Scale	72.6	65.5
9	Sludge	17.0	17.9
10	Sludge	Not detected	Not detected
11	Scale	629.7	403.1
12	Sludge	58.8	50.4
13	Sludge	50.3	58.3
14	Sludge	28.3	20.3
15	Sludge	58.6	40.6
16	Scale	2.6	1.78
17	Scale	1.1	0.90
18	Scale	1.6	1.2
19	Scale	15.2	41.5
20	Scale	0.8	0.86
21	Scale	302.2	67.4
22	Scale	0.4	0.56

As shown in Table III, ^{226}Ra concentration activities were quite variable, and ranged from 0.4 to 1,399.1 $\text{kBq}\cdot\text{kg}^{-1}$. The highest concentration activity values (1,399.1 $\text{kBq}\cdot\text{kg}^{-1}$; 1,272.6 $\text{kBq}\cdot\text{kg}^{-1}$, and 629.7 $\text{kBq}\cdot\text{kg}^{-1}$) were detected for samples 1, 6 and 11, respectively. Samples 1 and 6 were collected from barrels used to store the waste materials. According to information obtained from the technical staff, this waste came from a E&P station called “Jordão”, but the barrels had no identification about the origin of their contents. These samples were classified as sludge based only on their appearance and on the amount of oil present, not from chemical characterization. ^{228}Ra concentrations, on the other hand, varied between 0.56 and 742.6 $\text{kBq}\cdot\text{kg}^{-1}$. For the majority of the samples, the ^{226}Ra concentration activity was higher than the correspondent ^{228}Ra values. These results are in agreement with other studies [14,18,19].

Sample number 11, scale collected from the inner surface of produced water pipeline (from a E&P Unit called “Sítio Novo”), showed very high activity. This was expected, as in general, NORM concentrations are greatest in the scales and sludge that form in water-handling equipment [4]. Samples 3, 7, and 8 were also collected from produced water pipelines, but from a different E&P Unit (SZ II).

Samples 16 to 22 were all collected from different pipelines that carry the oil before any processing operations. In fact, they carry a mixture of oil, water and some gas that is extracted with the oil. Concentration activities for ^{226}Ra and ^{228}Ra were much lower for these samples, except sample number 21 (which came from the E&P Unit “Sítio Novo”).

This study is still in progress; more samples are being collected and analyzed to obtain a better understanding of the process of scale forming. Chemical and mineral analyzes are under way to get more information about scales and sludge collected from those E&P Units.

References

- [1] EPA. U.S. Environmental Protection Agency, Office of Radiation and Indoor Air, Radiation Protection Division, Washington, D.C., October 1999. Technical Report on Technologically Enhanced Naturally Occurring Radioactive Materials in the Southwestern Copper Belt of Arizona.
- [2] Vegueria, S. F. J., Godoy, J. M., Miekeley, N. Environmental impact studies of barium and radium discharges by produced waters from the “Bacia de Campos” oil-field offshore platforms, Brazil. *Journal of Environmental Radioactivity*, 62: 29 – 38, (2002).
- [3] Hebert, M. B.; Scott, L. M.; Zrake, S. J. A radiological characterization of remediated tank battery sites. *Health Physics*, 68(3): 406 – 410, (1995).
- [4] Smith, K. P., Blunt, D. L., Arnish, J. J. Potential radiological doses associated with the disposal of petroleum industry NORM via landspreading, prepared for U.S. Department of Energy, National Petroleum Technology Office, Tulsa, Oklahoma, by Argonne National Laboratory, Argonne, Illinois (1998).
- [5] Hamlat, M. S.; Kadi, H.; Fellag, H. Precipitate containing NORM in the oil industry: modelling and laboratory experiments. *Applied Radiation and Isotopes*, 59: 93 – 99, (2003).
- [6] Ceccarello, S., Black, S., Read, D., Hodson, M. E. Industrial radioactive barite scale: suppression of radium uptake by introduction of competing ions. *Minerals Engineering*, 17: 323 – 330, (2004).
- [7] Testa, C., Desideri, D., Meli, M. A., Roselli, C., Bassignani, A., Colombo, G., Fantoni, R. F. Radiation protection and radioactive scales in oil and gas production. *Health Physics*, 67(1): 34 – 38, (1994).
- [8] Rood, A. S., White, G. J., Kendrick, D. T. Measurement of ^{222}Rn flux, ^{222}Rn emanation, and $^{226,228}\text{Ra}$ concentration from injection well pipe scale. *Health Physics*, 75(2): 187 – 192, (1998).
- [9] Smith, A. L. Radioactive-scale formation. *Journal of Petroleum Technology*, June (1987).
- [10] White, G. J., Rood, A. S. Radon emanation from NORM-contaminated pipe scale and soil at petroleum industry sites. *Journal of Environmental Radioactivity*, 54: 401 – 413, (2001).
- [11] Wilson, A. J., Scott, L. M. Characterization of radioactive petroleum piping scale with an evaluation of subsequent land contamination. *Health Physics*, 63(6): 681 – 685, (1992).
- [12] Savonenkov, V. G., Smirnova, E. A., Trifonov, V. A. Occurrence of radium in deposits from petroleum waters. *Radiochemistry*, 39(1): 86 –89, (1997).
- [13] Zielinski, R. A.; Otton, J. K.; Budahn, J. R. Use of radium isotopes to determine the age and origin of radioactive barite at oil-field production sites. *Environmental Pollution*, 113: 299 - 309, (2001).
- [14] Godoy, J. M., Cruz, R. P. ^{226}Ra and ^{228}Ra in scale and sludge samples and their correlation with the chemical composition. *Journal of Environmental Radioactivity*, 70: 199-206, (2003).
- [15] HAMLAT, M. S., DJEFFAL, S., & KADI, H.. Assessment of radiation exposures from naturally occurring radioactive materials in the oil and gas industry. *Applied Radiation and Isotopes*, 55: 141-146, (2001).
- [16] Heaton, B., Lambley, J. TENORM in the oil, gas and mineral mining industry. *Applied Radiation Isotopes*, 46: 577-581, (1995).

- [17] Lysebo, I., Birovljev, A., Strand, T. (1996). NORM in oil production – occupational doses and environmental aspects. Proceedings of the 11th Congress of the Nordic Radiation Protection Society, Reykjavik, August 26–30, 1996, In: [http:// www.gr.is/nsfs_eng.html](http://www.gr.is/nsfs_eng.html), Access: 16 Oct. 2002.
- [18] Matta, L. E. S. C., Godoy, J. M. O., Reis, M. C. D., Pinto, R. S. M. Avaliação dos problemas radiológicos devido aos radionuclídeos naturais, em unidades de exploração e produção de petróleo. In: REGIONAL CONGRESS ON RADIATION PROTECTION AND SAFETY, 5., 2001, Recife – Brazil. Anais... Recife: IRPA/SBPR, 2001. 1 CD.
- [19] Steinhäusler, F., Paschoa, A. S., Zahorowski, W. Radiological impact due to oil- and gas extraction and processing: a comparative assessment between Asia-Pacific, Europe, and South America. In: IRPA – 10. Proceedings of the 10th International Congress of the International Radiation Protection Association, Hiroshima, 2000, edited by Japan Health Physics Society, Tokyo, Japan, 7 pages.
- [20] Hipkin, J., Paynter, R. A., Shaw, P. V. Exposures at work to ionizing radiation due to the use of naturally occurring radioactive materials in industrial processes. Appl. Radiat. Isot., 49(3): 205 – 209, (1998).
- [21] Blunt, D. L. Gooden, D. S., Smith, K. P. Issues related to setting exemption levels for oil and gas NORM. Technical Report for presentation at: The Six Annual International Petroleum Environmental Conference, November 16 – 18, 1999, Houston, TX, 11p.