Journal of Environmental Radioactivity 189 (2018) 202–206

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad

Geochemical signature of NORM waste in Brazilian oil and gas industry

G.T. De-Paula-Costa[a,*], I.C. Guerrante[a], J. Costa-de-Moura[a], F.C. Amorim[b]

[a] Department of Radioactive Waste Management and Transport, Brazilian Nuclear Agency (CNEN - Comissão Nacional de Energia Nuclear), General Severiano Street 82, 22290-901, Rio de Janeiro, RJ, Brazil

[b] Department of Mechanical Engineering, Federal Center for Technological Education of Rio de Janeiro, CEFET-RJ, UnED, Itaguaí, RJ, Brazil

ARTICLE INFO

Keywords:
Geochemical signature
Geochemical fingerprints
Radioactive waste management
Oil NORM
TENORM

ABSTRACT

The Brazilian Nuclear Energy Agency (CNEN) is responsible for any radioactive waste storage and disposal in the country. The storage of radioactive waste is carried out in the facilities under CNEN regulation and its disposal is operated, managed and controlled by the CNEN. Oil NORM (Naturally Occurring Radioactive Materials) in this article refers to waste coming from oil exploitation. Oil NORM has called much attention during the last decades, mostly because it is not possible to determine its primary source due to the actual absence of a regulatory control mechanism. There is no efficient regulatory tool which allows determining the origin of such NORM wastes even among those facilities under regulatory control. This fact may encourage non-authorized radioactive material transportation, smuggling and terrorism. The aim of this project is to provide a geochemical signature for oil NORM waste using its naturally occurring isotopic composition to identify its origin. The here proposed method is the modeling of radioisotopes normally present in oil pipe contamination such as ^{228}Ac, ^{214}Bi and ^{214}Pb analyzed by gamma spectrometry. The specific activities of elements from different decay series are plotted in a scatter diagram. This method was successfully tested with gamma spectrometry analyses of oil sludge NORM samples from four different sources obtained from Petrobras reports for the Campos Basin/Brazil.

1. Introduction

Among other nuclear and radioactive subjects, the Brazilian Nuclear Energy Agency (CNEN) controls the storage and transportation of radioactive waste. Naturally Occurring Radioactive Material (NORM) from oil exploration has been an issue along the last decades. Gas and oil exploration processes produce waste contaminated with NORM. The main concern with such NORM occurrences is the difficulty to determine the primary source of such waste, especially, in the absence of regulatory control. Such oil NORM occurs by precipitation or incorporation of these materials in the oil sludge, pipe cleaning, in scales inside pipes, vessels, heat exchanger, pieces of pumps, and others (Afifi and Awwad, 2005).

One of the main responsibilities of the CNEN as the official ruler is to develop efficient tools to control the radioactive waste in the country. Due to the dynamics and versatilities of gas and oil production as well as the amount of oil productive wells, it is hard to determine the origin of the many so-called NORM wastes produced by such facilities. Regarding this, the CNEN-8.01 act regulates as follows (CNEN, 2004):

> *Art. 42 All facilities must keep an updated record system of the radioactive waste, including:*
>
> *I – The radioactive waste type identification, origin and the location of its container;*
>
> *II – The radioactive waste origin and destination.*

Concerning waste management of oil production, "*the hazardous characteristics of such waste depend on the type of oil produced*" (Cunha, 2009). Thus, origin and provenance of oil wastes are extremely important subjects in determining the risk levels for the environment and the people.

Nowadays, there is already a serious regulatory control issue regarding metal scraps containing NORM. These scraps are sold by oil producers to scrap-dealers who resell the scrap to the steel industry. The steel industry has installed radiation detectors at the entrance access of their plants. Because of this the CNEN is constantly requested to verify and investigate warnings about the presence of radioactivity in steel oil tubes. In most of the cases it is impossible to identify the primary source of these scrap tubes contaminated with NORM and thus the effective control and notification of the primary seller cannot be done.

The goal of this project is to develop a geochemical signature for each specific NORM waste enabling to identify the radioactive waste source using its naturally occurring radiochemical components and support the CNEN in its activities of regulation. This article presents a

* Corresponding author.
E-mail addresses: gilberto.costa@cnen.gov.br, gilbertothiago2000@gmail.com, gilbertothiago@id.uff.br (G.T. De-Paula-Costa).

https://doi.org/10.1016/j.jenvrad.2018.04.014
Received 8 November 2017; Received in revised form 12 February 2018; Accepted 16 April 2018

Table 1
2014 and 2015 oil and natural gas volume production and proved reservoirs (CIPEG, 2016).

2014				
OIL in millions of barrels (MMbbl)		offshore	onshore	Total
	Production	**761.35**	**61.58**	**822.93**
	Proved reservoirs	**15,350.06**	**832.22**	**16,182.29**
NATURAL GAS in millions of cubic meter (MMm3)		offshore	onshore	Total
	Production	**23.,39**	**8.50**	**31.90**
	Proved reservoirs	**399,920.02**	**71,228.17**	**471,148.19**
2015				
OIL in millions of barrels (MMbbl)		offshore	onshore	Total
	Production	**831.30**	**58.37**	**889.67**
	Proved reserssvoirs	**12,366.90**	**666.34**	**13,033.70**
NATURAL GAS in millions of cubic meter (MMm3)		offshore	onshore	total
	Production	**26.74**	**8.39**	**35.13**
	Proved reservoirs	**358,702.31**	**70,754.75**	**429,457.10**

study on the project's viability based on literature data.

2. NORM in oil industry

2.1. Location of oil wells in Brazil

Brazil is the world's 12th largest oil producer (CIPEG, 2016). Brazilian production fields comprise onshore and offshore oil and gas wells spread out in all country territory. The biggest volumes are produced offshore. Table 1 shows the volume of oil and gas produced in 2014 and 2015. 93% of the oil and 76% of the gas produced in the country came from offshore plants. Besides that, pre-salt production represented 40% of offshore oil production in 2016. In addition, it is expected that many new wells start production in the near future (Petrobras, 2017).

2.2. Oil NORM history

Since the thirties the occurrence of NORM in the oil extraction tubes inlays is well known. It is usually associated with sulfate and carbonate of barium. During the seventies large companies sponsored research to evaluate risks relative to radon in oil production plants. In the eighties, researchers in the USA detected relatively high concentration of NORM in the oily inlays, scale and sludge coming from the oil platforms. Therefore, the US government and the oil industry initiated research to characterize and map the main locations where oil NORM occurs (Attallah et al., 2012).

In Brazil this issue started in the 80s, when Petrobras identified the presence of radiation in the oil sludge of pipes coming from the Namorado field (Campos basin). During many years Petrobras had to store pipes with NORM scales due to the absence of a cleanup technology for decontaminating such pipes. The problem continued until the early 2000s, when Petrobras developed a process to remove the inlays from the tubes. After this the scales and oil sludge were stored in barrels to attend the demands imposed by the CNEN (Matta and Reis, 2002). Nowadays, as already mentioned in section 1, the oil NORM wastes status inside the country is under control. However, the CNEN, as the only and official responsible of the government, still needs an appropriate tool that allows identifying the precise source origin of those wastes.

3. Geochemical signatures in nuclear regulation

The idea of geochemical signatures in nuclear applications is relatively new. Costa-de-Moura et al. (2013) and Costa-de-Moura (2009, 2013) determined geochemical signatures that indicate the provenance of columbite-tantalite (coltan) ores in Brazil. It was found out by modeling the relations (Nb/Ta; U/Th) that such elemental ratios provide fingerprints of the original source location of such ore. This result helps and allows the CNEN to improve the control of the economical circulation of those ores in the country.

Graupner et al. (2010) and Melcher et al. (2015), following an UN request to create a way to avoid the commerce of what is called “blood-coltan”, described geochemical signatures for coltan (columbite group minerals) ore mined in Africa. Combining U-Pb mass relations with associated rare earth elements (REE), geochronological data, REE ratios, and mineralogy they obtained individual signatures for coltan ore in Africa.

Balboni et al. (2016) presented a methodology for geochemical signatures of uranium ores demonstrating the importance of geochemical signatures in the investigation on the origin of intercepted nuclear material, both in local community or cross-border transport. This study provided a detailed chemical characterization of 11 samples of USA uranium ore. The authors plotted Th versus Y and U versus Th contents and the total REE concentration normalized to chondrite REE standards demonstrating that these chemical indicators can be used to distinguish depositional areas. The results showed the necessity of combining multiple chemical features to determine the origin of uranium ore.

El Mamoney and Khater (2004) applied a relation between ^{226}Ra and ^{228}Ra to determine the highest radiological impact zones involving oil industry and its waste of the Red Sea region, Egypt. The authors indicated the regions where radiological impacts would be bigger in case of accidents involving NORM waste coming from oil facilities in this region.

Yet, there is no methodology available in the literature for the determination of geochemical signatures in oil NORM waste. However, Shawky et al. (2001), in their work about oil NORM waste characterization in the oil industry in Egypt, concluded that each oil formation will produce distinct NORM waste with different NORM concentrations. The authors identified that the NORM waste characteristics depend not only on the extraction manner but mainly on the original characteristics and on the chemical arrangement of those elements in the mineral matrix. They also highlighted the importance of such knowledge for regulation and the development of management techniques for those wastes.

4. Method and materials

Here presented is a preliminary study based on literature data and on Petrobras gamma spectrometry analysis reports to verify the viability of a more complex project that, if continued, will include collection and multiple analyses of oil NORM samples.

The determination of radionuclides and the measurement of specific activities in the ^{238}U and ^{232}Th series is done by gamma spectrometry (Knaepen and Bergwer, 1995; Kolb and Woick, 1984). It consists of quantifying radioactive elements by gamma-ray emission spectrum using a high-purity germanium detector (HPGe). Below it is shown how some radionuclides are determined by this method:

Gamma-spectrometry for radioisotopes of the **^{238}U decay series**:

a ^{226}Ra is indirectly measured by the γ-emission peak of 609 keV and 1120 keV of the **^{214}Bi**.
b ^{210}Pb is directly determined by measuring its γ-emission of 46.5 keV.

Gamma-spectrometry for radioisotopes of the **^{232}Th decay series**:

a ^{228}Ra is indirectly measured by the γ-emission peak of 911.2 keV and 969 keV of the **^{228}Ac**;
b ^{224}Ra is indirectly measured by ^{212}Pb or ^{212}Bi.