Development of Microwave Technology for TENORM Waste Treatment-17377

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ABSTRACT

The sludge and scales generated by the oil and gas industry usually contain radionuclides of the thorium and uranium decay chains, the so-called technologically enhanced, naturally occurring radioactive materials (TENORM) waste. The handling of this waste must consider both the radiation risks presented by those radionuclides and its chemical toxicity, due to the decomposition of oil residues, which may generate hydrogen sulfide and other hazardous compounds. In the case of Brazil, Public Law 10.308 limits the management options for radioactive waste generated by offshore oil production rigs to drumming and storage; it prohibits disposal of any radioactive waste in seawaters, seabed or oceanic islands. This paper describes the results of the work to develop a treatment process using a specially designed microwave oven, which removes simultaneously water and hydrocarbons from the sludge, thus reducing the volume, the chemical toxicity and the chemical reactivity of the waste.

INTRODUCTION

The Nuclear and Energy Research Institute (IPEN-CNEN/SP) one of the Brazilian Nuclear Energy Commission research centers, conducts research and development work on characterization, treatment, conditioning and final disposal of radioactive waste. In 2016, IPEN-CNEN/SP started a project to study microwave technology for the treatment of the radioactive sludge generated by the oil and gas industry, in cooperation with Alliance Ambiental company.

The radioactive waste under study is generated in oil and gas production platforms. The extracted oil contains natural radioactive substances of the thorium and uranium decay chains, known as TENORM (Technologically Enhanced Naturally Occurring Radioactive Materials), which are separated and constitute a residue that must be removed from the extraction platforms.

TENORM waste is considered a radioactive waste when the concentrations of radionuclides of the thorium and uranium decay chains, mainly radium isotopes and their progeny, are above the legal limits; its chemical toxicity is due to the decomposition of oil residues, which may generate hydrogen sulfide and other hazardous compounds. The risks to operators or public individuals can be significantly higher when large amounts of this waste are drummed and stored offsite, instead of being, for instance, injected into the well bore during plugging and abandonment operations or re-injected by hydraulic fracturing. However, storage is unavoidable in the case of Brazil's offshore oil production rigs, because Public Law 10.308 forbids disposal of radioactive waste in the seawaters, subsea bed or oceanic islands, leaving long-term storage as the only alternative.

Sludge containing TENORM are continuously produced in oil platforms. It is a mixture of waste oil, wastewater, sand and other mineral matter that accumulates inside pipes, tanks and other equipment of the platform. Published data from Campos Basin platforms indicates that sludge is a chemically complex mixture of water, hydrocarbons and sediments. These wastes cannot be simply discarded because they have an activity concentration higher than the clearance levels established in the regulations of Brazilian Nuclear Energy Commission. Consequently, they are conditioned in drums, transported to the mainland and stored in warehouses by the producing companies.

The main radionuclides present are ^{226}Ra and ^{228}Ra and their concentrations range from 0.2 to 560 kBq kg^{-1}. However, concentrations of ^{226}Ra in the order of 1 MBq kg^{-1} were observed, with peaks of up to 26 MBq kg^{-1}.

The development of a treatment method for these wastes is necessary and timely. Currently, thousands of tons of sludge conditioned in drum are stored in 'initial storages' as defined by Law 10.308, without definition of final destination. A treatment for such wastes that removes hydrocarbons and water will result in the prevention of the generation of toxic gases (H_2S) and the corrosion of the drums, improving the long-term management safety.

The objective of this project is to study the application of microwave technology to remove water and hydrocarbons, ensuring that the removed materials are free of radioactivity so that water can be released without restrictions and the hydrocarbons are separated or burnt.

Once this treatment technology is developed and deployed, the oil and gas extraction industry will have an alternative for storing smaller and less dangerous volumes of waste.

Principles of the technology

Microwave is an electromagnetic radiation in the frequency range between 300 MHz and 300 GHz, but domestic or industrial ovens generally operate at 2.45 GHz frequency which corresponds to a wavelength of 12.2 cm and energy of 10.2 μeV.

Data from the literature indicate that microwaves have already been used as an energy source to treat and solidify hazardous and radioactive waste. In one of such process, the energy of a 60 kW generator, operating at 916 MHz, was directed through a waveguide into a drum in which the radioactive wastes were heated until they were melted at 1000°C. The volume was reduced by more than 80% and the resulting vitreous material met the regulatory requirements for final disposal as radioactive waste.

Microwave heating has a number of advantages in the treatment of various types of waste: significant volume reduction, rapid heating, the possibility of reaching high temperatures, selective heating of a few components of the wastes, flexibility for application without direct contact with the waste and with less risk to the operator, low cost and easy maintenance, lower energy consumption than other alternatives. Furthermore, the equipment can be portable and used *in situ*.

The use of microwave ovens for the pyrolysis of waste rather than incineration in conventional ovens avoids the formation of dioxin, furan and NOx compounds, so that the gases resulting from the process meet regulatory limits. The resulting solid residue generally consists of inert ash. But if ash treatment is required, they can be converted into glassy materials by the addition of glass-forming substances.

For radioactive waste from oil production, it is important to remember that Law 10.308 establishes in Article 7: "It is prohibited the disposal of wastes of any kind in the oceanic islands, the continental shelf and the Brazilian territorial waters." Therefore, the offshore oil extraction companies in Brazil are required to transport the sludge and other radioactive waste to the mainland and stored them in initial or intermediate storage, incurring in higher operational costs.

The development and deployment of a waste treatment technology, which is an alternative to the long-term storage of untreated waste, is therefore timely and have a high degree of environmental and occupational safety, because it is expected to reduce the waste volume and eliminate the dangers associated with the chemical decomposition of the waste.

Once the project is successfully completed, the oil extraction industries and regulatory authorities will have a technology that will help manage the long-term storage problem, since the current regulatory scenario is lack of definition of the waste final destination.

Project design

The objective of this work is to develop a technology for processing waste from oil and gas production platforms, whose content of natural radioactive substances classifies the waste as TENORM. The specific objectives are

- take representative samples of a sufficient number of waste drums currently stored in radioactive waste storages and characterize them with respect to the content of water and hydrocarbon, dissolved solids and total solids, sulfates, carbonates, sulfur, silica, Mg, Al, Ca, Mn, Fe, Zn, Sr, Ba and Pb, and the concentrations of ^{226}Ra and ^{228}Ra and other radionuclides;
- submit the samples to the microwave treatment, varying power, time of treatment and other operational conditions;
- measure the remaining water, hydrocarbons and solid contents of the samples after treatment and to measure the fraction of volatile substances recovered in the process;
- measure the activity concentrations in each fraction;
- collect quantitatively the gases and aerosols generated in the treatment process and analyze them in respect to the content of radionuclides;
- to scale-up the equipment to industrial scale.

The chemical and radiochemical characterization of the samples will be performed as described below:

- Concentrations of ^{226}Ra and ^{228}Ra and other radionuclides in waste samples and in the fractions collected during the treatment process will be determined by gamma spectrometry, preceded or not by radiochemical separation as required;

- The oil content will be determined by extraction in a Soxhlet apparatus using kerosene as the solvent. The residual organic matter will be determined by calcination at 500 °C up to constant weight;
- The content of carbonates, sulfur and silica will be determined by conventional chemistry methods and the Mg, Al, Ca, Mn, Fe, Zn, Sr, Ba and Pb elements will be determined by ICP-OES.

The microwave treatment tests will be carried out following the method:

- The TENORM material will undergo microwave drying in the apparatus shown in Figure 1, especially built for this tests;

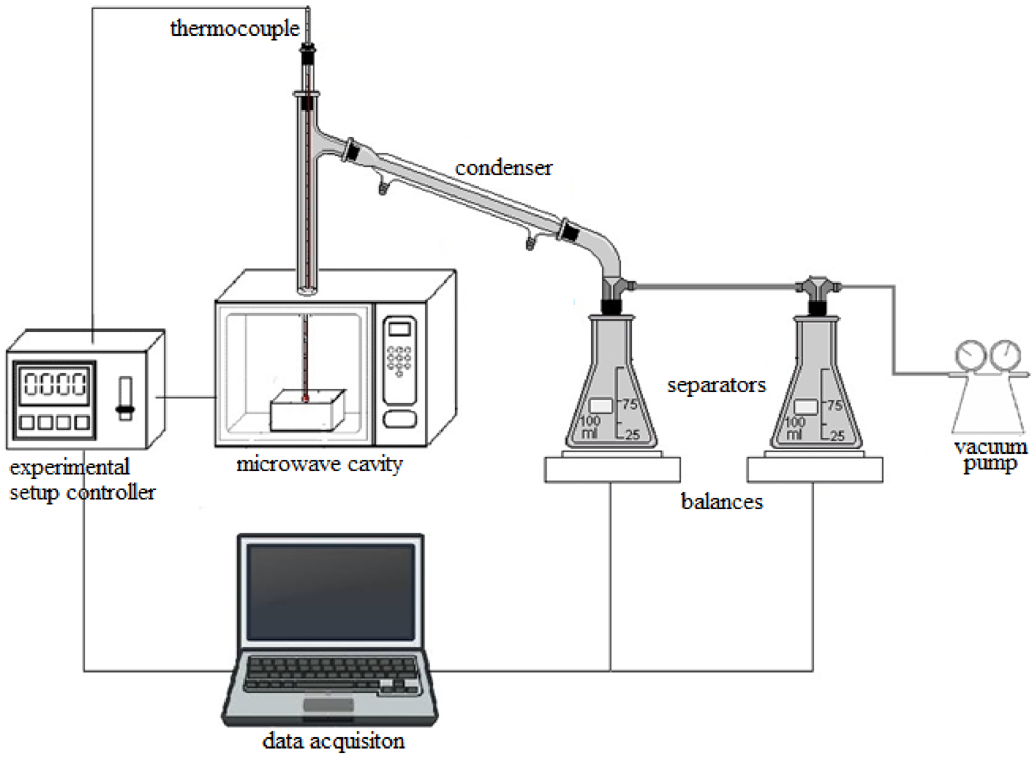

Figure 1 - Experimental Setup

- representative samples of TENORM sludge will be characterized, according to the method mentioned above, to allow the adjustment of the operating parameters of the Experimental Setup controller;

- Preliminary tests will be carried out with the different samples to obtain the limits of the operational parameters of the process, such as: heating rate, operating temperature and final moisture of the sample as a function of the time of exposure of the material within the Microwave cavity;

- A factorial experimental design will be performed, by varying the temperature and initial moisture of samples, each one in three levels, denoted by low (-1), medium (0) and high (+1), called the 3k factorial experiment. The drying system will be evaluated in two blocks: one with humidity below 50% and one with humidity above 50%. Tables 1 and 2 present the coded levels of the independent variables and the generic matrix of the factorial experiment 3^2

Table 1: Experiment levels

Factor	–1	0	1
X_1Temperature (ºC)	X_{11}	X_{12}	X_{13}
X_2 Humidity (%)	X_{21}	X_{22}	X_{23}

Table 2 – Planning matrix of the factorial experiment

Factors Number	Control Factors		
	X_1	X_2	Response (y_i)
1	+1	+1	y_1
2	+1	-1	y_2
3	+1	0	y_3
4	-1	+1	y_4
5	-1	-1	y_5
6	-1	0	y_6
7	0	+1	y_7
8	0	-1	y_8
9	0	0	y_9

The responses or dependent variables (yi) may be multiple, will be defined by the research group, and may be the physical and/or radiochemical condition of the condensed evaporated material and/or the physical and radiochemical condition of the material remaining in the microwave cavity.

The results will allow carrying out an operational optimization of the process to indicate the best operating conditions of the system, which produces the best result within the evaluated range.

Waste sample characteristics

The waste sample is composed of five 200 L-drums with approximately 1,000 kg total mass, containing absorbent materials, sand and other soil materials, water and oil, in pH 6 approximately. Previous results show that the waste contains about 3 $g.kg^{-1}$ of unresolved complex mixture (UCM) of hydrocarbons and about 4 $g.kg^{-1}$ of total petroleum hydrocarbons (TPH). The ^{226}Ra content varied between less than 1 and a few hundred Bq g^{-1}.

A preliminary assessment of the radioactivity content of the whole waste drums indicates that the total activity concentration is about 25 $kBq.kg^{-1}$ and that ^{226}Ra is the main radionuclide present. Dose rates on contact vary between 3 and 7 $\mu Sv.h^{-1}$. Visual inspection revealed heterogeneous samples, shown in Figure 2

Figure 2: Samples of TENORM sludge

Final Remarks

Large amounts of NORM waste exceeding the clearance level of 10 $Bq.g^{-1}$ of ^{226}Ra, ^{228}Ra and other thorium- and uranium-decay chain radionuclides are generated as a result of onsite decontamination of topside equipment. Onsite decontamination results in the removal of accumulated sludges from separators and systems handling produced water. Different disposal alternatives of NORM waste from the oil and gas industry such as re-injection by hydraulic fracturing together with cuttings and other types of production waste, injection into the well bore during plugging and abandonment operations, disposal in an abandoned mine, tunnel or other types of underground facilities are unavailable in the country because of legal restrictions.
Presently, the only available alternative is long-term storage until regulators decide on the final destination of the waste, most probably the land disposal by burial with encapsulation by a concrete barrier.

Volume and mass reduction of the waste and elimination or reduction of the hazard represented by the presence of water and hydrocarbons is acknowledge under those circumstances. The treatment of the waste by microwave drying is expected to fulfil the above objectives.