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TREATMENT OF TENORM WASTE USING SURFACTANT

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ABSTRACT

The petroleum industry is responsible by the generation of wastes that are both toxic and radioactive, sometimes called mixed waste. The toxicity is due to the presence of hydrocarbons and sulfur and the radioactivity is the result of the leaching of thorium and uranium daughters present in the oil-producing formation and their transport by the extracted fluids to the production rigs. Because of the presence of these radioactive materials of natural origin, this waste is named TENORM (Technologically Enhanced Naturally Occurring Radioactive Material). The main radionuclides present are ^{210}Pb, ^{224}Ra, ^{226}Ra and ^{228}Ra. In Brazil, the offshore platforms cannot dispose this waste by reinjection in wells because federal law prohibits disposal of radioactive waste in seawaters or seabed. The waste is, therefore transported to land and stored. This work aims at investigating a method of decontaminating the oil sludge by using surfactant that can increase the removal efficiency of the radionuclides. After a successful treatment, the decontaminated waste can be disposed of as non-radioactive industrial waste in a licensed facility and the concentrated radioactive material can be treated as radioactive waste, decreasing significantly the costs of management and improving safety.

1. INTRODUCTION

Extraction of oil from underground reservoirs is accompanied by considerable amounts of oil sludge and scales, making these a major problem for the oil industry. This waste is classified as Technologically Enhanced Naturally Occurring Radioactive Material, TENORM, by the presence of radioactive elements that occur naturally in the oil producing formations. In the Brazilian regulation, this waste is classified as Class 2.2 radioactive waste, whose disposal in the sea, seabed and oceanic islands is prohibited by law. The only management option for the radioactive waste generated in offshore rigs is transportation to onshore storage facilities. Due to its expressive generation, the interest in finding alternative methods to reduce the volume of the waste has grown, in order to benefit the industrial sector with the reduction of energy costs and with a possible mitigation of environmental impacts.

The major contributors of natural terrestrial radiation are the isotopes of the natural radioactive series of thorium (^{232}Th) and uranium (^{235}U and ^{238}U), as well as the radioisotope of potassium (^{40}K). However, the daughters of thorium and uranium series ^{224}Ra, ^{226}Ra and ^{228}Ra are the more soluble and under certain physical and chemical conditions they leach from the reservoir rock and are transported to the surface, so they remain in the produced waters and in the storage-tanks bottom sludge, or they co-precipitate in pipe walls forming the pipe scales [1].

Long-term storage of these wastes poses an occupational risk to workers and to individuals of

the public. Therefore, it is important to seek methods for removing the radionuclides prior to storage of the oil residues. The methods with greater potential are the use of inhibitors of sludge and scales, leaching and extraction using different solutions [2]. Removal of radionuclides present in the TENORM seems to be feasible and could be applied in the country to solve the problem of storage and final disposal of these wastes.

This work aims at investigating a method of decontaminating the oil sludge by using inorganic solvents and surfactants to achieve an efficient removal of the radionuclides.

2. MATERIALS AND METHODS

Oil sludge samples removed from the bottom of storage tanks of a Floating Production Storage and Offloading (FPSO) platform in the State of Rio de Janeiro, provided by Shell Petroleum, were used in the experimental run. Samples from five drums of oil sludge were previously dried in oven at 80ºC, homogenized and stored prior to the decontamination tests.

Aliquots of the solid fraction were characterized by scanning electron microscopy (SEM). A JEOL system, model JSM-7401F Field Emission Scanning, was used to provide information on the morphology and identification of chemical elements.

The surfactant solutions were prepared by diluting concentrated Triton X100 in water at room temperature to the concentrations of 2.5% and 5% in volume.

Six different samples were treated with two concentrations of the surfactant Triton X100.
The main variables that influence decontamination process are surfactant concentration, contact time and sample temperature. Each tested sample was left at room temperature for about 30 minutes and then homogenized. Samples of about 25 grams were weighed in analytical balance in previously tare weighted plastic bottles of 200 mL, and 110 mL of surfactant solution added. The mixtures were shaken for intervals ranging from 30 to 90 minutes, at temperatures of 25°C, 40°C and 55°C.

After treatment, samples were centrifuged and the supernatant separated. The solid fraction was hermetically sealed in a petri dish and stored for four weeks to establish the secular equilibrium between the target radionuclides and their respective daughters, and then counted in a hyperpure germanium gamma spectrometer. A Canberra Gamma Spectrometry system, model GX2518, with HPGe detector and Genie 2000 software, was used for data acquisition and processing.

3. RESULTS AND DISCUSSION

Graphs of the remaining activity in the solid fraction as function of the time of contact, surfactant concentration are shown in Figures 1 and 2.

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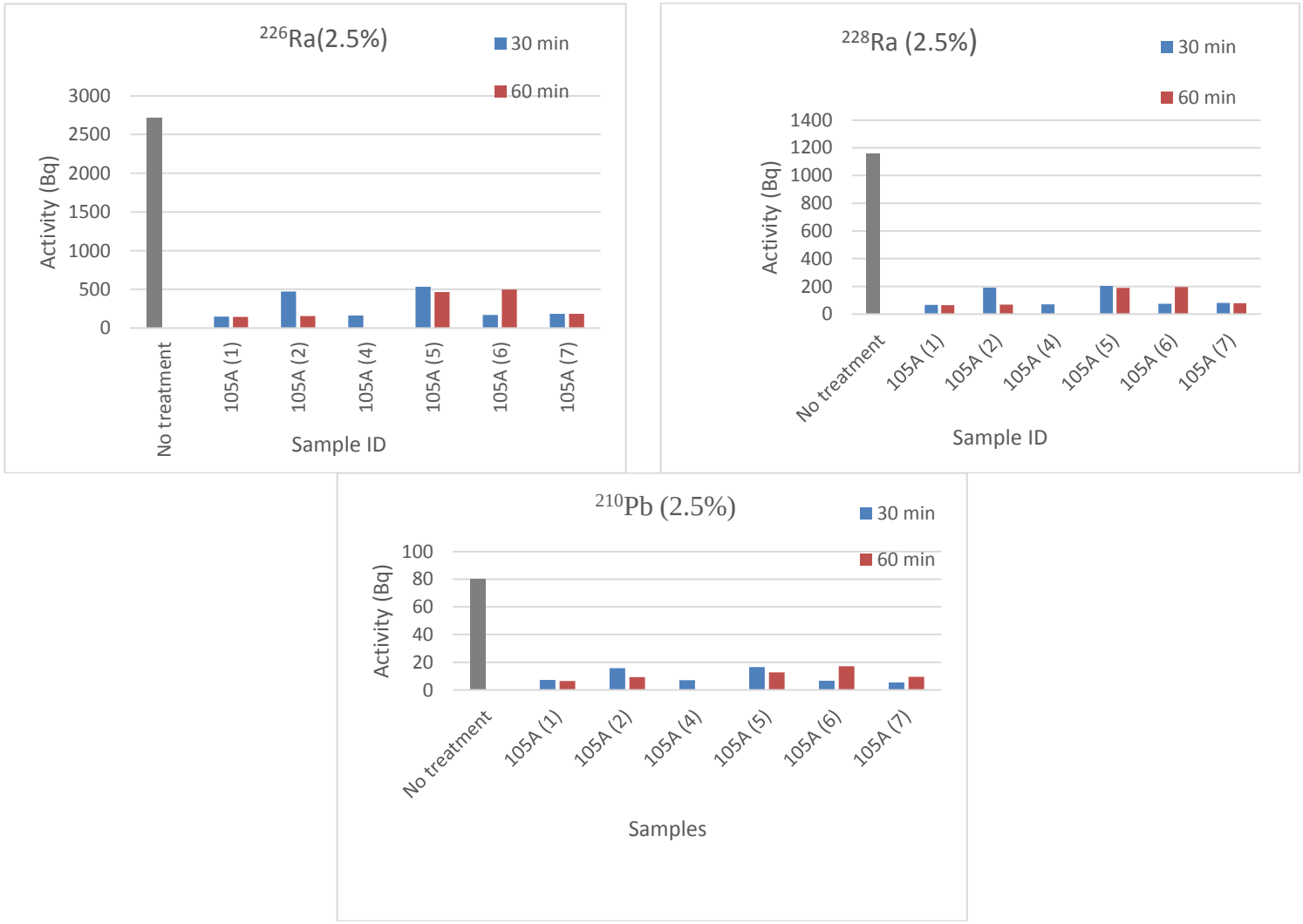

Figure 1: Decontamination experiments with 2.5% surfactant concentration: ^{226}Ra, ^{228}Ra and ^{210}Pb.

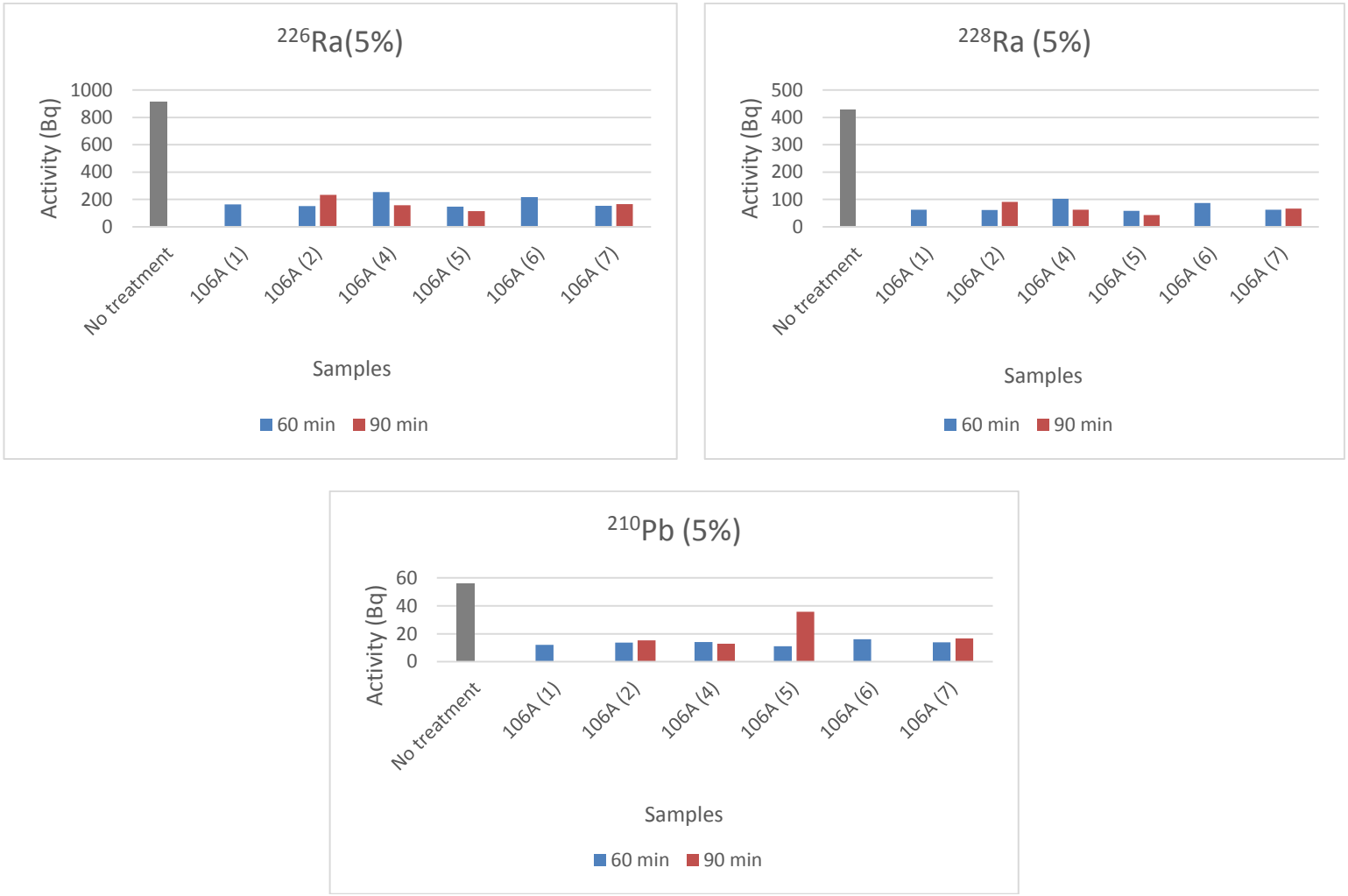

Figure 2: Decontamination experiments with 5% surfactant concentration: ^{226}Ra, ^{228}Ra and ^{210}Pb.

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Table 1: Treatment of residues using surfactant in concentration of 2.5%

Radionuclides	No treatment (Bq/ sample)	Concentration (%)	Treatment with surfactant $\bar{x}$ (Bq/ sample)	
			30 min	60 min
^{226}Ra	2605	2.5	278	290
^{228}Ra	1126		114	119
^{210}Pb	80		17	16

Table 2: Waste treatment using surfactant an 5%

Radionuclides	No Treatment (Bq/sample)	Concentration (%)	Treatment with surfactant $\bar{x}$ (Bq/sample)	
			60 min	90 min
^{226}Ra	2605	5	181	168
^{228}Ra	1126		72	65
^{210}Pb	80		13	20

As shown by data in Table 1 and Table 2, it can be observed that the use of surfactant in concentrations of 2.5% and 5% were satisfactory.

The removal percentage of the radionuclides present in the oil sludge was between 75% and 94%. The contact time of the sludge with the solvent in the period of 30 minutes, as well as in an hour, had little influence on the result.

These results are in agreement with those presented in the literature, in which percentages up to 84% of removal were found [3].

3.1. Oil sludge characterization result by SEM

It is known that in its composition the sludge contains heavy metals, oil, water, oxides and clay mixture. This material in contact with the metal receptacle walls promotes oxidation reactions due to permanent contact, changing the original characteristics of the waste over time.

Therefore, it was possible to obtain the result of the interaction between an electron beam and the atomic structure of the sample, and through this interaction the topography of the sample surface could be constructed. Figures 3 and 4 are examples of images obtained from both the sludge sample without treatment and with treatment with surfactant.

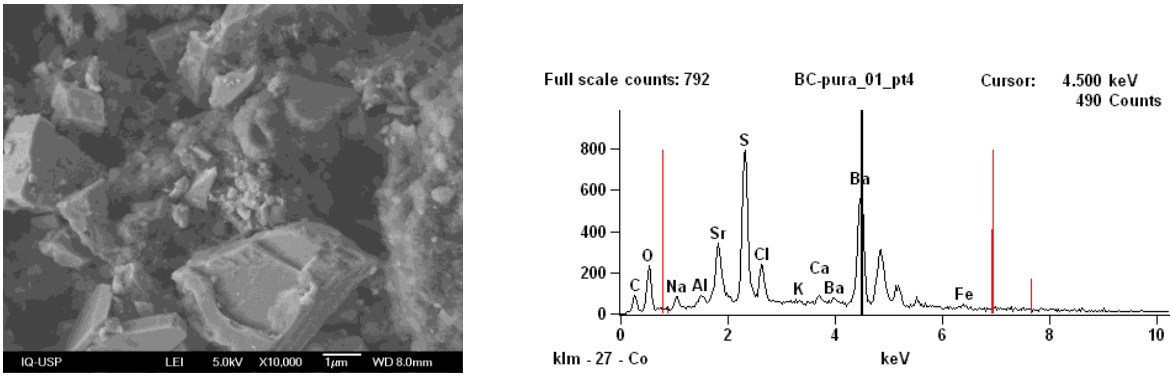

Figure 3: Pure composite sludge without treatment

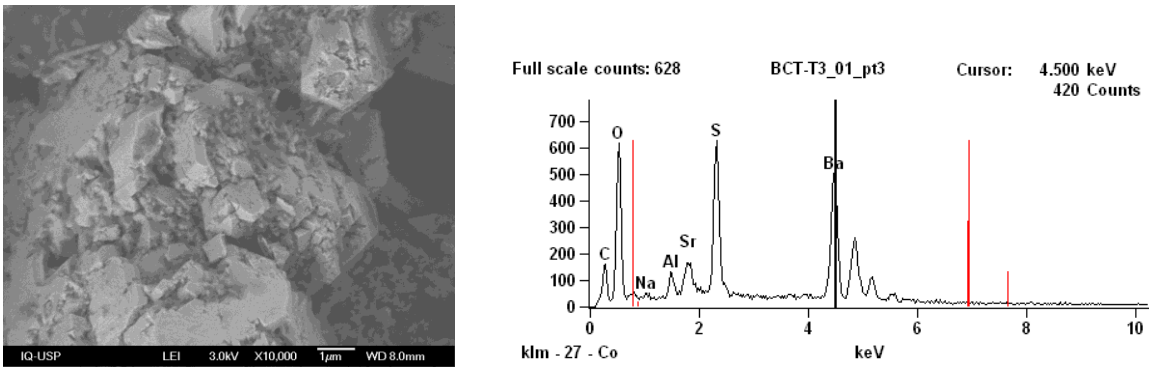

Figure 4: Composite sludge treated with surfactant

In general, micrographs, with a magnification of 10.000 times show that the materials are made up of very fragmented and irregular particles, both in size and morphological (surface) aspect, presents non-uniform fibers, as described by Zhao and others [4].

Table 3: Metals presents in raw sludge by Energy Dispersion Spectroscopy (EDS)

	C-K	***O-K***	***Na-K***	***Al-K***	***Si-K***	***P-K***	***S-K***	***Cl-K***	***Ca-K***	***Fe-K***	***Ba-L***
Raw Sludge	40.96	45.36	3.52	0.32	0.44	0.46	2.62	1.87	0.23	2.10	2.12

EDS is a qualitative and quantitative X-ray microanalysis technique that can provide information on the chemical composition of a sample for atomic number (Z) elements > 3.

In Table 3, EDS indicated the presence of metals: sodium, aluminum, calcium, iron and barium; and nonmetals: silicon, phosphorus, sulfur and chlorine. Alkaline and alkaline earth metals react easily with oxygen to form oxides.

Aluminum (Al) is not an element intrinsically linked to petroleum, but is usually found in the soil in ores in the form of alumina (Al_2O_3). This is a possible explanation for the strong presence of the chemical element in the analyzed samples [5].

Table 4: Metals presents in treated sludge by EDS

	C-K	*O-K*	*Al-K*	*S-K*	*Ca-K*	*Sr-L*	*Ba-L*
Treated Sludge	35.35	50.25	0.53	6.95	0.18	1.39	5.35

In Table 4, it was possible to observe that even the materials presenting non-uniform and irregular fibers, with the use of surfactant these particles were more packed. However, the microstructural analyzes by EDS spectra indicate distinct compounds rich in barium and sulfur, this particle probably being barium sulfate ($BaSO_4$).

4. CONCLUSIONS

The method used to achieve the removal of the present radionuclides from the petroleum sludge has been optimized with the use of the surfactant solvent as the main removal agent.

The results obtained in the experimental tests presented a high efficiency removal for ^{226}Ra, ^{228}Ra and ^{210}Pb. As well as the respective EDS spectra indicated distinct compounds rich in barium, sulfur and strontium, probably being barium sulfate ($BaSO_4$) and strontium sulfate ($SrSO_4$). This barium sulfate is associated with water that comes out mixed with petroleum in the extraction process.

The presence of sodium can characterize a fuel adulteration by water contaminated by this metal, while calcium and barium metals can characterize the presence of motor oil in oil sludge as being components of the oil formulation with the property of maintaining an alkaline reserve the same [6].

Therefore, new experiments should be conducted in order to establish treatment conditions for large volumes, but we can conclude that this process of decontamination may be a good solution for the oil and gas industries to treat this type of waste.

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