BJRS

BRAZILIAN JOURNAL
OF
RADIATION SCIENCES
09-01A (2021) 01-16

Preliminary studies on electron beam irradiation as a treatment method of radioactive oil sludge

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ABSTRACT

Radiation-induced advanced oxidation processes have been proposed for the treatment of various types of wastes. However, electron beam technologies for the removal of recalcitrant compounds in petroleum wastes are still poorly understood. This work aims at evaluating the effects on the degradation of organic matter from oil sludge by electron beam irradiation. Characterization methods were employed to identify the chemical elements present in the waste. Radiometric analysis was performed to identify radionuclides and measure dose rates. Preliminary immobilization of the untreated waste with cement indicated resistance values very close to the minimum established in national regulation. To treat the waste, an electron beam accelerator, model Dynamitron II, with variable current up to 25 mA was employed and the irradiation doses ranged from 20 to 200 kGy. Solutions were prepared with an initial H_2O_2 concentration of 1.34 mol·L^{-1}. The effects on the removal of total organic carbon are discussed.

Keywords: **Oil sludge, Electron beam, Radioactive waste.**

ISSN: 2319-0612

Accepted: 2020-11-09

1. INTRODUCTION

Petroleum extraction activities produce oil sludge wastes that are frequently classified as Naturally Occurring Radioactive Materials (NORM) since they contain radioactive daughters from thorium and uranium decay chains. Oil sludge is composed of extracted sediments, water, and hydrocarbons that accumulate in tanks, pipes, and other structures in oil production rigs. In addition to containing radionuclides in radiologically significant concentrations, the sludge produced in Brazilian offshore platforms has high concentrations of sulfur [1, 2] that represents a problem for the storage of such waste. The problem is related to the formation of corrosive sulfuric acid that damages the drums where the waste is stored and the formation of hydrogen sulfide that is a very toxic, corrosive, and flammable gas [3].

The interest in developing methods for the treatment of this type of waste is increasing, since its accumulation in large quantities and with significant levels of activity in the onshore storage facilities poses a growing health risk to workers and the local population. Currently, there is no legal guidance for the disposal of this radioactive waste in Brazil. Article Seven of Federal Law No. 10,308 of 2001 prohibits disposal of radioactive waste in the sea or seafloor, thus prohibiting reinjection of NORM waste generated in oil platforms into abandoned wells [4]. Furthermore, current regulations allow the disposal of oil sludge in landfills only for wastes containing radionuclides at concentrations below unrestricted clearance levels. Oil sludges with activity below clearance levels are treated by encapsulation with oleophilic bentonite and disposed of in industrial landfills [5].

While no decision is taken on disposal routes, the amount of drummed, radioactive oil sludge is increasing, posing threats to human health as a result of its toxicity, flammability, and corrosivity. Consequently, Brazilian oil companies are seeking a method to reduce the volume and the toxicity of the stored NORM waste.

One treatment method already tested has proved satisfactory from the point of view of effectiveness, cost, and environmental protection for non-radioactive sludge [6, 7]. After transport to onshore facilities, treatment aims at reducing waste hazards, such as mixing the sludge with the oleophilic bentonite in powder form to encapsulate the sludge. The encapsulant has the function of

forming a permanent physical barrier that avoids leaching of toxic products to the environment, especially into groundwater [8] when the waste is disposed of in landfills.

There are a number of other methods that can be used to improve the treatment and removal of organic compounds that are pollutants and toxic agents. However, most of them do not achieve the required performance in eliminating or reducing the impact of disposal into the environment or are not cost-effective. This points out the need for alternative methods, which can be used separately or in combination, to improve treatment efficiency.

Considering parameters such as costs, yield, and operation time, as well as the impacts on the environment, advanced oxidation processes (AOPs) have presented good results and are shown as an attractive alternative to be explored in waste treatment. Recently, some studies have employed ozonation to degrade the organics and promote physicochemical modifications in a Brazilian oil sludge [9]. The results were promising, indicating that this AOP technique is an interesting alternative to the treatment of this material.

The use of electron beam irradiation (EBI) is considered an AOP and it is an emerging technology for industrial waste treatment. EBI was previously used in the treatment of industrial effluents, showing excellent results with almost 90% removal of organic compounds [10,11]. However, to the best of our knowledge, the use of EBI to degrade organic compounds in oil sludge has not been yet investigated.

In this study, a Brazilian oil sludge is characterized in terms of organics content, and identification of elements and radionuclides. Furthermore, electron beam irradiation after the addition of H_2O_2 in the radioactive oil sludge is discussed regarding the effects of irradiation doses on the degradation of organic compounds.

2. MATERIALS AND METHODS

2.1. Preparation and characterization of the samples

Oil sludge was received in three (3) plastic 200-L drums from a petroleum platform of the Campos Oil Field. Samples from the three drums were homogenized individually before collecting representative aliquots from each one for the irradiation assays. Sample S1 presented supernatant

liquid, while samples S2 and S3 had no free liquid, but noticeable moisture. A fourth composite sample named SC was created (Figure 1) by mixing equal amounts of samples S1 to S3. The liquid phase of drum 1 (see Table 1) was also considered and named SL. SL is a mixture of water and oil, but mainly water. The liquid was poured in a separation funnel, but no significant phase separation was observed. All samples were transferred to the laboratory and stored under refrigeration (4º C) until use. Table 1 details the different types of samples investigated.

Figure 1: *Petroleum sludge (SC sample).*

Table 1: Separated phases or mixed samples collected from three waste drums.

Name of the sample	Source	Material type	Moisture (%)[a]
S1	Drum 1	Wet solid	52
S2	Drum 2	Solid	33
S3	Drum 3	Solid	38
SC	Drums 1-3	Wet solid	45
SL	Drum 1	Liquid	–

[a] Measured in a moisture analyzer (Ohaus, USA) at 120 °C for 60 min.

2.2. Preparation and characterization of the samples

EBI breaks the O−H bond in water molecules by radiolysis, generating various oxidizing species, including $^{\bullet}OH$, $H^{\bullet}$, and solvated electrons (e^{-}_{aq}). EBI can also transform H_2O_2 into $^{\bullet}OH$ and H_2O, generating large amounts of hydroxyl radicals by coupling both H_2O_2 homolysis as well as water radiolysis. When the oxidizing species formed interact with organic molecules, they oxidize the matter followed by dissociation and degradation into CO_2 and H_2O [10].

The electron beam accelerator, Radiation Dynamics Inc., emits electrons of 1.5 MeV with a current range from 1 mA to 25 mA. The electron beam scans an area of 60 cm long per 4 cm wide at a frequency of 100 Hz. The samples were prepared with 3.3 mm thickness, in order to achieve a proper penetration of the electron beam through this waste. Table 2 shows the experimental conditions used.

Table 2: Conditions of electron beam irradiation of oil sludge samples.

Sample ID	Experimental condition	Added volume of H_2O_2 (mL)	Irradiation dose (kGy)
A	Raw sludge	–	200
B	H_2O_2 (1.34 mol L^{-1}) added	10	100
C	H_2O_2 (1.34 mol L^{-1}) added	10	200

Scanning Electron Microscopy (SEM) and Energy-dispersive Spectroscopy (EDS) analysis were carried out in an electron microscopy HITACHI TM3000, with a tungsten source and acceleration voltages of 5 and 15 kV, and electron beam resolution of 30 nm. Images were acquired with magnification from 1,000 to 30,000 times. Samples were dried in oven at 80 °C and compacted in the form of disc pellets for these analyses.

Inductively coupled plasma optical emission spectrometry (ICP/OES) (Optima 7000DV, PerkinElmer, USA) was employed to identify the chemical elements present in oil sludge. Three aliquots of the SC sample were heated on a plate for about two weeks. During this time interval, concentrated acids were added, HNO_3 (98-99%) H_2SO_4 (95-97%), and HF (48-52%), to dissolve the waste. After dryness, addition of HNO_3 was made twice, so that the samples were prepared to ICP/OES analysis. Calibration solutions were prepared by dilution of certified standard solutions (Johnson Matthey, UK).

Total organic carbon (TOC) was measured to evaluate organic compounds mineralization. The samples were analyzed using a Shimadzu TOC-L equipment, coupled to an autosampler (ASI-L) and a solid combustion chamber (TOC-5000A). TOC was measured indirectly by the difference between total carbon (TC) and inorganic carbon (IC).

Samples were dried in oven at 80ºC and compacted in the form of disc pellets. The piece of equipment used was the HITACHI TM3000 MEV. Acceleration voltages of 5 and 15 kV; tungsten source; magnification of 15 to 30,000× and resolution of 30 nm.

Cadmium zinc telluride (CZT) semiconductor detector, Kromek Raymon10, was used for gamma ray spectrometry and dose rate measurement. The energy resolution and energy interval were setup between 2.0-2.5% full width at half maximum (FWHM) and from 60 keV to 3 MeV, respectively. The counting time was 72,000 seconds. To confirm that the portable CZT detector was capable of routinely and quickly identify gamma radiation emitters in the waste, the more accurate, non-portable HPGe detector with a beryllium window of 0.5 mm thickness was used (Canberra Industries, model GX4510). The detector shielding was composed of lead, copper and lucite walls, 105-mm, 2-mm, and 4-mm thick, respectively.

2.3. Immobilization method of the untreated oil sludge

The immobilization method performed was similar to a procedure detailed elsewhere [12]. In short, oil sludge was solidified in cement to evaluate its loading capacity. The oil sludge/cement ratio evaluated was 0.30 (w/w) without any pH adjustment. The specimens were prepared in disposable plastic molds, 5 cm diameter and 10 cm height. The cement paste was premixed, transferred to the plastic molds, and held sealed for 28 days at 22 °C.

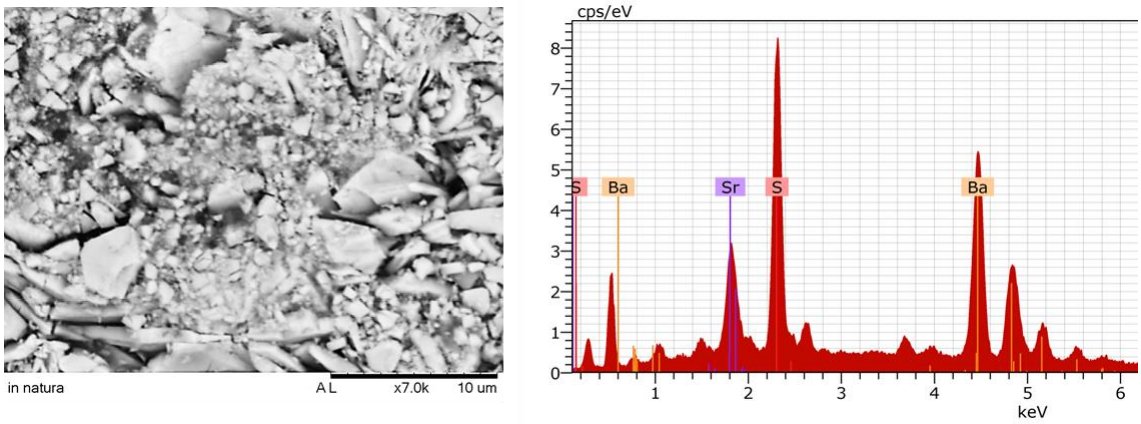
The parameters evaluated were the free liquid after 24 h, setting time, and mechanical strength. A Vicat needle was employed to determine the setting time. Six samples were evaluated for each determination.

3. RESULTS AND DISCUSSION

Prior to samples irradiation, characterization of the oil sludge was performed. The characterization included ICP/OES, scanning electron microscopy (SEM), EDS, presence and identification of radionuclides, and total organic carbon.

Figure 2 shows a micrograph of the dry oil sludge surface, as well as the identification of the elements present in this sample by EDS. The micrograph depicts the heterogeneity of the sludge, with no clear definition of particle size or shape. Furthermore, it indicated discontinuous layers of materials placed one upon another, with few empty spaces and no hollows.

Figure 2: *Micrograph of the surface of dry oil sludge and identification of the elements present by EDS.*



The oil sludge in study presented significant amounts of Ba, Sr, and S. No difference was observed in SEM/EDS analysis for the treated oil sludge (results now shown). EDS is accurate in evaluating small fractions of the material of interest. However, to better evaluate the whole material, ICP/OES was also employed, especially to determine the elements in the liquid portion of the waste. These elements are listed in Table 3.

Table 3: Identification of the elements present in the oil sludge by the ICP/OES.

Element	**Concentration (mg L^{-1})**
Sr	175.85
Fe	159.20
Ca	39.40
Zn	12.70
Ba	10.61
Mg	9.76
Cu	6.08
Cr	3.44
Ni	2.07
Mn	1.93
Li	0.20
Pb	0.13
Ga	0.08
Co	0.06
Cd	0.03

Table 4 shows the radionuclides identified, which are those expected in this type of waste. The contact dose rate for 100 g was 5 μSv h^{-1} for the raw sludge. The measurement was made with the detector very close to the flask with sludge. As for the dose rate, the level of radioactivity is between medium to high for the oil sludge patterns.

The analysis performed with the Raymon10 handheld detector could not yield conclusive values for the activities. Nevertheless, it can be employed for faster monitoring routines. The identified isotopes were ^{208}Tl, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi, and ^{228}Ac. The result of ^{228}Ac is used to determine ^{228}Ra and the results of ^{208}T1, ^{212}Pb and ^{212}Bi to determine ^{228}Th. To confirm the presence of ^{226}Ra and ^{210}Pb, further analysis was made by using a Canberra gamma detector, which is expected for this variety of waste. ^{228}Ra was also measured, but indirectly by ^{228}Ac. Table 4 lists the concentration of such radionuclides, as well as ^{40}K.

Table 4: Activities found for ^{226}Ra, ^{228}Ra, ^{210}Pb, and ^{40}K, for each sample

Sample	Nuclide name	Wt mean activity (Bq)[α]
S1	^{226}Ra	2720 ± 37
	^{228}Ac	1159 ± 20
	^{210}Pb	80 ± 17
	^{40}K	< DL[β]
S2	^{226}Ra	910 ± 14
	^{228}Ac	426 ± 8
	^{210}Pb	56 ± 10
	^{40}K	< DL
S3	^{226}Ra	1094 ± 12
	^{228}Ac	511 ± 8
	^{210}Pb	99 ± 23
	^{40}K	< DL
SL	^{226}Ra	0.78 ± 0.69
	^{228}Ac	0.39 ± 0.07
	^{210}Pb	0.77 ± 0.16
	^{40}K	3.90 ± 0.79

α: X ± S (mean ± standard deviation); β: Detection limit.

The isotopes measured and those inferred by the decay chain require adequate disposal as radioactive waste because they are in the "medium-upper" group of radiotoxicity as indicated in Table 5, which presents dose coefficients for public exposure (DCPE) as a surrogate of a scale of radiotoxicity. Note that the limits for exemption for radionuclides and the limits for clearance of radioactive waste containing those radionuclides are inversely proportional to radiotoxicity, while the dose coefficient per unit intake is proportional to the radiotoxicity. In view of this, the classification was based on DCPE values. In comparison with groups one and three, the second group is then in the medium-upper radiotoxic group and to complete the scale it is important to point out that there are still three groups of radionuclides with dose coefficient in the range of 10^{-9}, 10^{-10} and 10^{-11}, that is, up to four orders of magnitude below Group 2.

Table 5: Dose coefficients for public exposure as a proxy of radiotoxicity for ^{226}Ra, ^{228}Ra, ^{210}Pb, identified in the samples. Data collected from [13].

Group 1 – medium		**Group 2 – medium-upper**		**Group 3 – upper**	
Fission products	**DCPE (Sv Bq^{-1})**	**Radioelements in oil sludge**	**DCPE (Sv Bq^{-1})**	**Highestradiotoxicity radionuclides**	**DCPE (Sv Bq^{-1})**
^{90}Sr	2.8×10^{-8}	^{210}Pb	6.9×10^{-7}	^{210}Po	1.2×10^{-6}
^{131}I	2.2×10^{-8}	^{226}Ra	6.9×10^{-7}	^{227}Ac	1.1×10^{-6}
^{137}Cs	1.3×10^{-8}	^{228}Ra	2.8×10^{-7}	^{250}Cm	4.4×10^{-6}

Although the raw oil sludge was irradiated in its entirety, TOC measurements were carried ou with both phases separately. The main reason is that the TOC content of solids must be made with dry materials, due to restrictions of the equipment used (TOC analyzer).

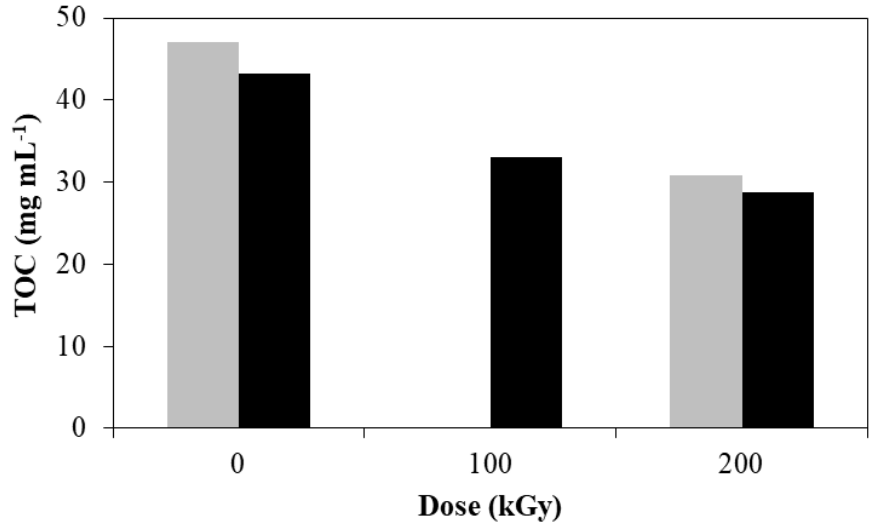
Figure 3(A) shows the behavior of the TOC removal obtained in the solid portion of the oil sludge. The irradiation of the raw oil sludge decreased the TOC of the solid fraction from 47.1 to 30.8 mg g^{-1}. The addition of H_2O_2 (1.34 mol L^{-1}) slightly increased TOC removal (28.7 mg g^{-1}) compared to raw sludge. Clearly, there is an indication that higher doses promote higher TOC removals, particularly when H_2O_2 is used. However, care must be taken, since it is not clear if this

process was enhanced by the addition of water, favoring homolysis, or by the break of H_2O_2 into hydroxyl radicals. It is worth observing that water homolysis also promotes the formation of H_2O_2, which may have been formed when irradiating the raw, wet oil sludge. The results so far also indicate that TOC removal does not follow a linear behavior with dose, with a much higher removal occurring from 0 to 100 kGy than that observed from 100 to 200 kGy.

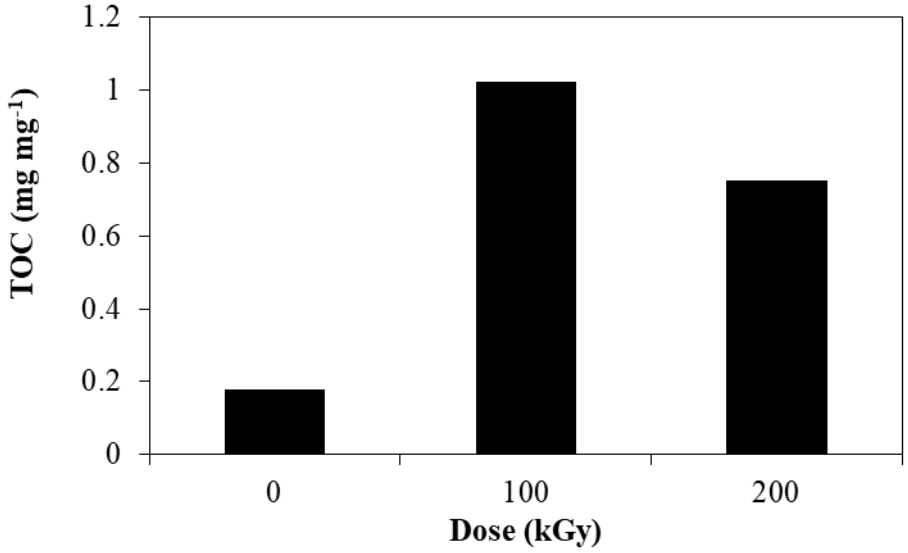
A different behavior was observed for the liquid phase (Figure 3(B)). The TOC content increased from 0.2 to 1 mg mL^{-1} under 100 kGy, and decreased from 1 to 0.8 mg mL^{-1} under 200 kGy. An increase in TOC content of the liquid phase is expected, since, under irradiation, the organics present in the solid portion may break into small, water-soluble or oil-soluble compounds. Consequently, the concentration of organic compounds in the liquid phase increases. The increase of dose promoted a decrease in TOC content, indicating that a fraction of the organics could have been decomposed into $CO_2 + H_2O$.

Figure 3: *TOC measurements. (grey) Raw sludge; (dark) Raw sludge + H_2O_2. (A) solid phase; (B) liquid phase. Inorganic carbon corresponded to less than 2% of the total carbon.*

A



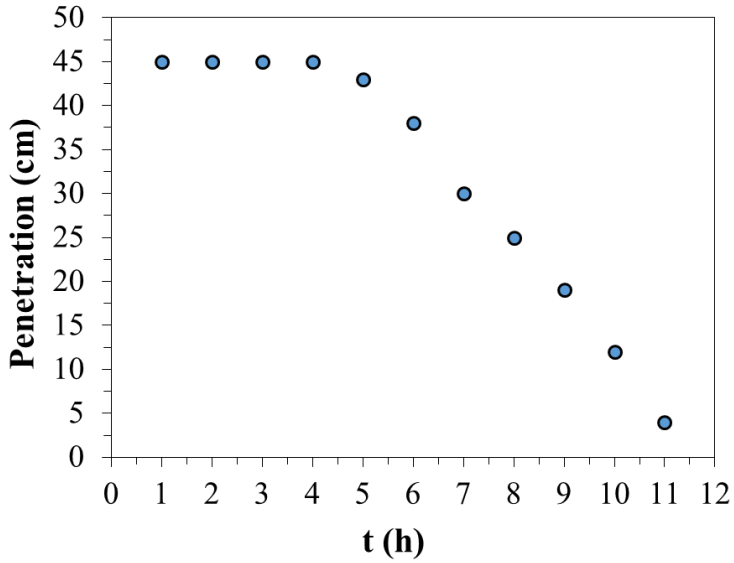
B



Finally, a preliminary investigation on the immobilization of oil sludge was conducted, using only the raw oil sludge. Parameters such as free water, setting time and resistance to axial

compression were evaluated. Free water was observed for most of the samples, but the segregated water volume was lower than 0.5%. Good workability of immobilization mixtures and no segregation of phases were observed for all samples before the final setting time. Figure 4 shows the hardening evolution over 11 h. After this time interval, the Vicat needle was no longer able to penetrate the sample, thus indicating 11 h as the final setting time.

Figure 4: *Hardening of oil sludge mixed with Portland cement.*



As regards mechanical resistance, all test samples presented mechanical resistance above 10 MPa (13.9 ± 0.8 MPa), indicating that the immobilization of raw oil sludge with Portland cement would fulfill the Brazilian acceptance criteria of the current regulation [14]. Further investigation with the treated oil sludge is still needed to evaluate if the immobilization process would be improved, with faster setting times and higher mechanical resistance values.

4. CONCLUSION

The electron beam irradiation (EBI) of real matrices is a complex process, since many chemical reactions occur simultaneously, such as AOP-based processes (H_2O_2/catalysts). Moreover, the presence of both inorganic (e.g., NO_3^-, HCO_3^-, PO_4^{3-}, etc.) and organic (dissolved organic matter, DOC) constituents may either promote or inhibit the degradation of the target compounds, as a result of the generation and/or scavenging of reactive species, respectively.

Additionally, direct EBI formation of by-products by all the aforementioned processes undoubtedly affects the kinetics and mechanism of sludge degradation. Further investigation is needed, aiming at a complete characterization of the target residue, as well as an in-depth study on the kinetics for this system.

EBI was able to decrease the TOC content of the solid phase, from 47.1 to 30.8 mg g^{-1}; the use of H_2O_2 (1.34 mol L^{-1}) did not result in significantly increasing TOC removal, reaching 28.7 mg g^{-1}. For the liquid phase, TOC increased as a result of the degradation of the organics present in the solid portion. Under a higher dose (200 kGy), the TOC content decreased, indicating that the organics could have been decomposed into CO_2 + H_2O. However, the mechanisms are still under consideration as a result of the matrix complexity. A significant higher removal occurred from 0 to 100 kGy than from 100 to 200 kGy.

The preliminary investigation on the immobilization of oil sludge by the cementation method was conducted with only the raw oil sludge. Although the results of mechanical resistance were above 10 MPa (13.9 ± 0.8 MPa), we assume that the TOC removal as a result of EBI application may enhance resistance. Faster setting time is also foreseen for the treated waste.

Despite the low dose rate of the samples, the isotopes measured and those inferred by the decay chain are in the "medium-upper" group of radiotoxicity, requiring adequate disposal as radioactive waste.

Finally, future work is needed to evaluate the effectiveness of the pre-disposal treatment concerning toxicity removal, costs, and eventually the usefulness for compatibility with immobilization matrices.

ACKNOWLEDGMENT

The authors thank the support given by the Center for Lasers and Applications' Multiuser Facility (IPEN-CNEN/SP) and Elisabeth S.R. Somessari of the Radiation Technology Center (IPEN-CNEN/SP) for the irradiation of the samples.

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