



Sequential chemical treatment of radium species in TENORM waste sludge produced from oil and natural gas production

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ABSTRACT

This paper is dedicated to the treatment of sludge occurring in frame of the Egyptian produced from oil and gas production. The activity levels of three radium isotopes: Ra-226 (of U-series), Ra-228 and Ra-224 (of Th-series) in the solid TENORM waste (sludge) were first evaluated and followed by a sequential treatment for all radium species (fractions) presented in TENORM. The sequential treatment was carried out based on two approaches 'A' and 'B' using different chemical solutions. The results obtained indicate that the activity levels of all radium isotopes (Ra-226, Ra-228 and Ra-224) of the environmental interest in the TENORM waste sludge were elevated with regard to exemption levels established by IAEA [International Atomic Energy Agency (IAEA), International basic safety standards for the protection against ionizing radiation and for the safety of radiation sources. GOV/2715/Vienna, 1994]. Each approach of the sequential treatment was performed through four steps using different chemical solutions to reduce the activity concentration of radium in a large extent. Most of the leached radium was found as an oxidizable Ra species. The actual removal % leached using approach B was relatively efficient compared to A. It is observed that the actual removal percentages (%) of Ra-226, Ra-228 and Ra-224 using approach A are 78 ± 2.8 , 64.8 ± 4.1 and $76.4 \pm 5.2\%$, respectively. Whereas in approach B, the overall removal % of Ra-226, Ra-228 and Ra-228 was increased to $\sim 91 \pm 3.5$, 87 ± 4.1 and $90 \pm 6.2\%$, respectively.

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1. Introduction

The TENORM waste is acronym for the 'technically enhanced naturally occurring radionuclide materials' produced from several industrial sectors such as uranium mining overburden, phosphate ore processing, coal ash, water treatment, metal mining and processing, geothermal energy production wastes, and petroleum industry [2]. In oil and gas production, the TENORM may be solid waste as scale and/or sludge and produced waters. The available data of the recent literature show that TENORM contain activity concentrations of Ra-226 ranged from undetectable levels to 1000 kBq/kg [3]. The activity concentrations of Ra-226 in TENORM can be much higher than the exemption levels established by IAEA [1]. The recommended exemption level for uranium-series is U-238 = 1 Bq/g and Ra-226 = 10 Bq/g. For thorium decay a chain is Th-232 = 1 Bq/g, Ra-228 = 10 Bq/g and Ra-224 = 10 Bq/g.

In the last decade, attention was focused on the environmental and health impacts from the uncontrolled release of

TENORM wastes [4–6]. Therefore, the treatment of these wastes is of increasing interest because accumulation of large amounts with a significant activity may cause health risks to the workers through exposure, inhalation of radon (Rn-222) decayed from radium and/or ingestion of waste dust during the periodical maintenance of the equipment used. The trials towards the treatment of TENORM wastes from many industries are still limited. The commonly used methods include subsurface disposal options, volume reduction, use of scale and/or sludge inhibitors, recycling, and leaching using chemical solutions [7–9]. In this concern, removal of Ra-226 from TENORM wastes produced from oil and gas industry was carried out by a simple extraction process using saline solutions (i.e., seawater) and chemical solutions [10,11]. Radium (Ra-226) content in the TENORM waste (PG: phosphogypsum) associated with phosphate processing was also treated using different chemical solutions by a simple extraction method [12]. Treatment of Ra-226 in Indian PG was carried out using two solutions: distilled water and rainwater under different conditions [13]. The present work describes the development of a sequential treatment for radium in sludge, to reduce its activity concentration consequently the health hazard potential to the workers in oil and natural gas production fields. The proposed treatment method was carried out on the basis of two

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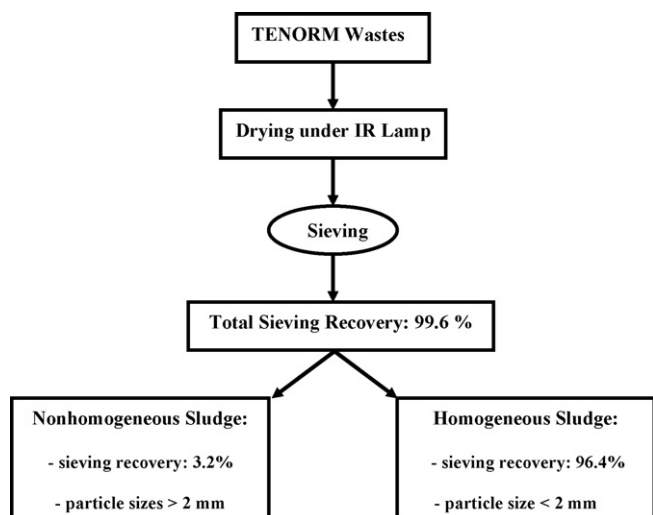


Fig. 1. Drying and preparing of the sludge waste samples produced from the petroleum exploration processes.

approaches using chemical solutions through four successive steps.

2. Experimental

2.1. Samples

The TENORM wastes are precipitated on the bottom and around walls of the storage tanks, due to the depression in temperature and pressure. These materials are precipitates of metal and radionuclides salts as well as organic residues, the sludge. Since the TENORM sludge and/or scale reduce the efficiency of the tanks storage, it is removed periodically during the maintenance process. The sludge represents wastes accumulated in large amounts (several hundred tonnes) surrounding workers in sites of the petroleum exploration. Therefore, 12 samples of the waste sludge are taken and collected in several plastic bags to prevent cross-contamination for radiometric investigation. The TENORM waste samples were obtained from the Abu Rudies onshore oilfield at the eastern bank of the Suez Gulf, South Sinai Governorate, Egypt.

2.2. Preparation of TENORM samples

Initially, the collected TENORM samples were screened in atmospheric air (25–30 °C) for 2 weeks. Then, the samples were dried under IR lamp for 1 week till complete dryness and constant weight. The dried sludge was crushed, pulverized and sieved using a programmable sieving vibratory (model: Analysette, Germany) into two main parts, namely: nonhomogeneous and homogeneous waste sludge. The total recovery of the sludge sieving reached up to 99.6%, while the rest of 0.4% represented a loss as dust released into atmosphere. The nonhomogeneous sludge was discarded due to its coarse particles greater than 2 mm and low sieving recovery of 3.2%. The homogeneous sludge has a particle size less than 2 mm and sieving recovery of 96.4%, therefore it is used for further investigation. Fig. 1 shows the procedure for drying and sieving of the waste sludge. An accurate 50 g of the homogenous dried sludge samples were packed in polyethylene bottles (volume: 100 cm³), sealed tightly by molten wax to prevent radon escape (to attain secular equilibrium) and stored more than 4 weeks before the radiometric measurements for the activity concentration assessment of radium isotopes (Ra-226, Ra-228,

and Ra-224) of the environmental interest present in the TENORM waste sludge.

2.3. Reagents and solutions used

All the chemicals and reagents used in the present work were of analytical grade (AR, Merck, Darmstadt, Germany). The chemicals and reagents were used without further purification. The solutions used were prepared using bidistilled water, while their acidity was adjusted using a microprocessor pH-meter with an accuracy of ± 0.05 (model: HANNA pH 211 Instruments, Portugal).

The treatment experiments were carried out with solid-liquid ratio of 1/5 (w/v) with continuous stirring for a sufficient time and a suitable temperature according to the proposed approach (case by case for each step). An accurate 25 g of the TENORM sludge batch (in polyethylene bottles, 100 cm³) and was used to state the net counts ($A_0 = c/s$) before leaching. 50 g of the sludge waste (of the same batch) was mixed with the leachant solution used for treatment in polyethylene bottles (400 cm³). The solid residue and solution phases were centrifuged at 3000 rpm for 5 min and separated carefully by filtration onto Whatman filter No. 42 (England) under suction pump. The separated nondissolved residue of TENORM after each step was dried in an electric furnace at 105 °C till constant weight. Then, 25 g of the dried residue in polyethylene bottles (100 cm³) was measured by γ -ray spectrometry to determine the net counts ($A = c/s$) after leaching. The samples before and after leaching were counted for 5 h using γ -ray spectrometry under the same conditions (i.e., $G = 1$).

2.4. Description of the experiment

The sequential leaching of the radium content in TENORM was based on the individual extraction for each Ra species in the waste, according to the successive four steps [14]. In this concern, five samples of a homogenized waste sludge (described previously) weighing 50 g were taken for leaching investigation in each approach. The sludge samples with leaching solutions were conditioned and experimented in polyethylene bottles of 400 cm³.

Approach A, the waste was leached using 20% of magnesium chloride solution (acidity: pH 7, temperature: 50 ± 1 °C, shaking: 1.5 h) to extract the water-soluble and exchangeable radium species (step A.1). The residue was leached again using 1 M sodium acetate/acetic acid solution (acidity: pH 5, room temperature, continuous agitation for 5 h). After 2 h of leaching the acidity of the solution was re-adjusted again to pH 5 using diluted acetic acid solutions (step A.2). The aim of this step is to leach the Ra fraction bounded to carbonate species (acidic fraction of Ra). The remained solid waste from the previous step was leached using a mixture of 0.04 M hydroxylamine hydrochloride/25% acetic acid solution with occasional agitation at 95 ± 2 °C for 6 h (step A.3), to leach the radium species bounded to metal-oxides such as the Fe–Mn-oxides [15]. The residue from last step was leached through two sub-steps: (I) the sample was leached using acidic oxidizing agent (hydrogen peroxide/ 7.5×10^{-3} M nitric acid solution, pH 2, 85 ± 2 °C, continuous agitation for 5 h) and (II) the residue from the last sub-step, was leached using a mixture of 3.2 M ammonium nitrate/20% nitric acid solution with agitation for half an hour (step A.4). The used solutions extracted the radium species bounded to organic matter and sulphides. The whole procedure is presented in Fig. 2A.

For approach B, 50 g of the sludge waste was treated sequentially using different chemical solutions, through main four leaching steps [16]. The waste samples were leached using de-aerated deionized water (pH 6.7) at the ambient room temperature (25 ± 1 °C) with the continuous agitation for 4 h, followed by leaching using 1 M ammonium acetate solution (pH 6.8, 25 ± 1 °C, 4 h, continuous

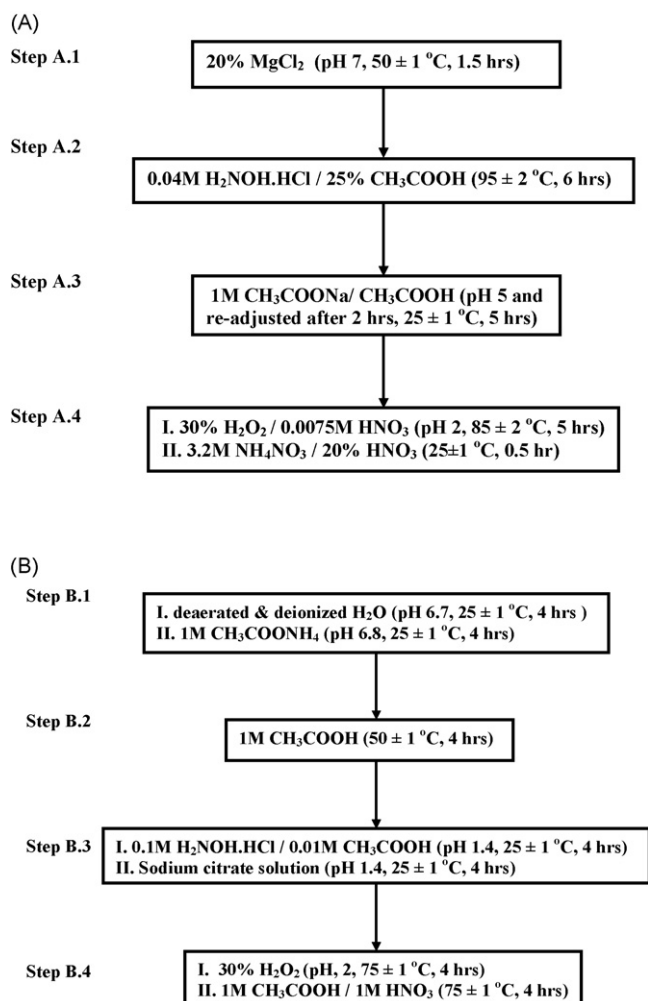


Fig. 2. (A) Leaching scheme of approach 'A' for sludge treatment and (B) leaching scheme of approach 'B' for sludge treatment.

stirring) to leach the exchangeable Ra species, such as the interstitial water and water-soluble species of Ra present in the waste (step B.1). The waste residue was leached again using 1 M acetic acid solution (50 ± 2 °C, continuous stirring, 4 h), to remove the acidic radium species as carbonates as well as some iron and manganese oxides (step B.2). The solid remaining of the waste was leached through two successive sub-steps using: (I) mixture of 0.1 M hydroxylamine hydrochloride/0.01 M acetic acid solution with acidity of pH 1.4 and (II) sodium citrate solution (step B.3). These solutions are selective for the reducible radium species in the waste, such as readily reducible species, manganese oxides, amorphous iron oxide and moderately reducible phase. The residue of the waste samples were leached using acidic solution of hydrogen peroxide followed by a hot mixture of 1 M acetic acid/1 M nitric acid solution (step B.4), to leach the available radium bounded to the organics and/or sulphides. The whole leaching steps of approach 'B' is summarized in Fig. 2B.

2.5. Radiometric measurements

The prepared samples for the chemical treatment investigation were done nondestructively using γ -ray spectrometry (detector: high purity germanium-HPGe (Oxford, TN Nucleus, Oak Ridge, USA), model: ERDS 30 20200, serial no.: 2201, bias supply: -3400 V, relative efficiency: 20%, resolution (FWHM): 2.0 keV at 1.332 MeV

for Co-60). The data acquisition was collected by 8 K multichannel analyzer (MCA) using software of Genie 2000. A sealed point source containing 0.1 μ Ci of Na-22, Co-60, Ba-133 and Cs-137 was used for energy calibration. The efficiency calibration was done using certified reference soil and sediment streams containing well-known activity concentrations of naturally occurring radionuclides, e.g. uranium, thorium and radium. The certified materials used are IAEA-312, -313, and -314 and purchased from the International Atomic Energy Agency, Vienna, Austria [17–19]. These samples are cylindrical sources (homogeneously distributed activity with constant volume and distance) placed coaxially with the detector for efficiency determination and the same procedure was applied for sample measurements.

For determination the activity concentration of Ra-226, Ra-228 and Ra-224, the dried sludge samples were packed in polyethylene bottles identical to those containing reference material obtained from AQCS/IAEA [17–19]. The samples were compacted to the same density as that of the IAEA reference materials. The samples were stored for 30 days to achieve secular equilibrium between radon (Rn-222) and its short-lived progenies (Pb-214 and Bi-214) in equilibrium with radium.

Activity concentration of Ra-226 was calculated based on the net count rate (c/s) of the radium progenies at 351.9 and 609.3 keV for Pb-214 (yield per decay of 35.8%) and Bi-214 (45%), respectively [20,21]. Activity concentrations of Ra-228 and Ra-224 were calculated based on the net count rate (c/s) at 911.1 (29%) and 238.6 (45%) keV, respectively. The samples were counted for 2 h. The minimum detectable activity (MDA) was calculated as follows using Curie equation [22]:

$$\text{MDA (Bq/kg)} = \frac{1.645 \sqrt{C_b}}{\epsilon p_\gamma t m} \quad (1)$$

where 1.645 is the value of the statistical coverage factor of σ (95% confidence level of σ), C_b is the counts of background, ϵ is the relative efficiency of HPGe-detector used, p_γ is the photopeak emission intensity (%), t is the counting time in s, and m is the sample weight (dry weight, kg). The MDA values for Ra-226, Ra-228 and Ra-224 were 1.2, 0.9 and 0.8 Bq/kg, respectively. The uncertainties arise due to a number of factors like volume of samples, efficiency calibrations, peak area determination and random uncertainties associated with background and sample counts. The combined uncertainties of all these factors did not exceed 7% for Ra-226, Ra-228 and Ra-224. To validate the analysis method, certified reference samples (AQCS/IAEA-312 and IAEA-313) of known activities are measured [18,19]. The activities of these samples were in agreement with their certified values within errors not exceeding 10%.

While for the leaching percentage (%) calculations, 25 the sludge waste before treatment equals to that obtained after each leaching step were measured using the γ -ray spectrometry for 5 h used to determine the net count rate (c/s) before (A_0) and after (A) leaching, respectively. Hence, the removal percentage (%) of Ra-226, Ra-228 and Ra-224 after each treatment was calculated according to the following equation [10]:

$$\text{removal (\%)} = \frac{A_0 - A}{A_0} \times 100 \quad (2)$$

where A_0 is the net count rate (c/s) of the sludge waste samples before treatment and A is the net count rate (c/s) of the sludge waste samples after treatment. The leaching percentage (%) of Ra-226 was evaluated directly based on its gamma photopeak at 186.2 keV (3.29%). The leaching percentages of Ra-228 and Ra-224 were calculated from the net counts of the photopeaks measured at 911.1 keV (29%) and 238.6 keV (45%), respectively [21].

3. Results and discussion

3.1. Activity concentration of Ra species in sludge waste

Before the treatment investigations, the activity concentrations of the main three radium isotopes were measured. It is found that the average activity level of Ra-226, Ra-228 and Ra-224 were $11,950 \pm 1700$, 1750 ± 200 and 1900 ± 250 Bq/kg, respectively. Since the TENORM wastes are accumulated in huge amounts and show high activity concentrations health hazards are released to the environment and the workers. Therefore, treatment approaches are suggested to reduce the human and environmental hazard potential.

3.2. Treatment investigation

It has been established that the environmental behavior and toxicity of trace elements and radionuclides depend strongly on their physicochemical forms (i.e., speciation) in the environment and in this respect radium is not excepted [23]. Therefore, the applied treatments involve four steps achieved sequentially for each approach. This allows to the selective extraction of the different classes of radium species present in TENORM waste, such as water-soluble species, exchangeable, carbonates, reducible species, oxidizable organics, etc.

3.2.1. Approach 'A'

The sequential leaching of the radium content in TENORM was based on the individual extraction for each Ra species in the waste, according to the successive four steps (A.1–A.4). The obtained results are presented in Table 1.

The exchangeable radium species was extracted and removed from the waste. The obtained removal percentages (%) of Ra-226, Ra-228 and Ra-224 are 5.7 ± 2.4 , 6.5 ± 1.4 and $3.1 \pm 0.9\%$, respectively. This value is high and comparable to the exchangeable Ra species present in and extracted from phosphate ores [24]. In the next leaching step (A.2) the results show that the removal percentages (%) are found to be of 9.9 ± 0.4 , 7.5 ± 0.9 and $11.8 \pm 0.2\%$ for Ra-226, Ra-228 and Ra-224, respectively. The leached part represents the Ra fraction bounded to carbonate species (acidic fraction of Ra). In step (A.3), it is found that the removal percentages of Ra-226, Ra-228 and Ra-224 are 10.9 ± 1.4 , 18.3 ± 2.5 and $19.6 \pm 0.4\%$, respectively. The removed radium species represent the released Ra fraction bounded to metal-oxides such as the Fe–Mn-oxides [15]. The residue of radium species bounded to organic matter and sulphides was leached through two sub-steps (A.4). The obtained removal percentages of Ra-226, Ra-228 and Ra-224 are 51.5 ± 2.1 , 32.5 ± 4.1 and $41.9 \pm 5.2\%$, respectively.

According to approach A, the successive leaching steps released most of the possible radium species present in the treated TENORM waste. The individual and overall removal percentages through all steps of approach A are presented in Table 1. It is observed that the actual removal percentages (%) of Ra-226, Ra-228 and Ra-224 are 78 ± 2.8 , 64.8 ± 4.1 and $76.4 \pm 5.2\%$, respectively. The variation in the removal % for each Ra-isotope may be due to the radiochemical factors such as the differences in their half-lives. On the other hand, Fig. 3 shows the leachability of the different Ra species in the waste. It is observed that the oxidizable Ra species is the main Ra fraction in this type of waste. This may be attributed to the high strength of the used leaching solutions to remove Ra species within the TENORM sludge waste. It is also showed that the reducible species of Ra-226 is in comparison with Ra-228 and/or Ra-224. Therefore, the radium species in the treated waste using approach A can be ordered as

oxidizable > reducible > acidic > exchangeable.

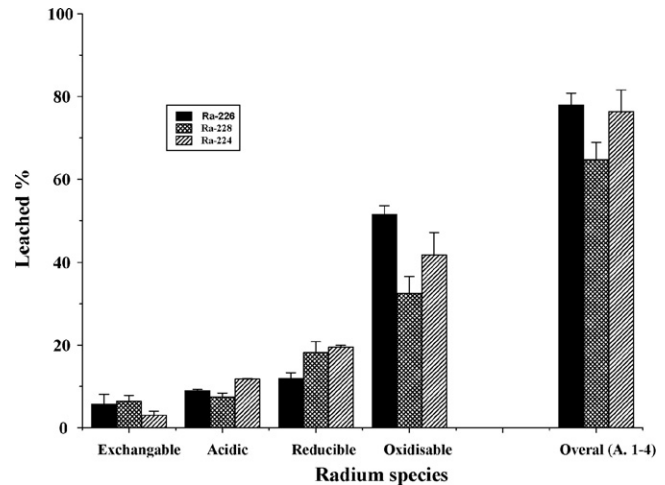


Fig. 3. Distribution of radium species in TENORM sludge using approach 'A'.

3.2.2. Approach 'B'

In this approach, the TENORM waste was treated sequentially using different chemical solutions, through main four leaching steps. The results of the approach are presented in Table 2. Initially, the water-soluble and the exchangeable Ra species are leached. The results showed that the leached percentages (%) of radium isotopes are 10.6 ± 1.5 , 9.7 ± 1.2 and $11.2 \pm 0.8\%$ for Ra-226, Ra-228 and Ra-224, respectively (step B.1).

In the next leaching process (B.2), the acidic radium species as carbonates as well as some iron and manganese oxides are removed. The obtained leaching percentages (%) of radium species are 12.8 ± 2.8 , 15.2 ± 0.5 and $16.5 \pm 1.2\%$ for Ra-226, Ra-228 and Ra-224, respectively. The solid remaining of the waste was leached through two successive sub-steps (I and II). The used solutions are selective to the reducible radium species in the waste, such as readily reducible species, manganese oxides, amorphous iron oxide and moderately reducible phase (step B.3). The obtained removal percentage (%) of Ra-226, Ra-228 and Ra-224 are 14.2 ± 1.2 , 17.4 ± 3.1 and $19.0 \pm 1.5\%$, respectively. Finally, the waste was treated using oxidizing reagent solution, as a selective chemical agent to leach the oxidizable radium species in the waste (step B.4). The leached percentages (%) of the oxidizable Ra species are 53.3 ± 1.2 , 48.4 ± 1.9 and $45.0 \pm 2.3\%$ for Ra-226, Ra-228 and Ra-224, respectively.

Based on the previous leaching sequence using selective chemical solutions for the different radium species present in the TENORM waste. The obtained results for the individual and total leaching percentages (%) of the different naturally occurring radium isotopes are cited in Table 2. It is showed that the overall removal percentages (%) of all radium species are 90.9 ± 3.5 , 86.7 ± 4.1 and $89.7 \pm 6.2\%$ for Ra-226, Ra-228 and Ra-224, respectively. These values indicate that there is a negligible variations in amounts of the leached the three radium isotopes by this approach. Fig. 4 represents distribution of the actual removed percentages (%) towards type of the radium species present in the treated waste. It is indicated that the high removal percentage of Ra-226 obtained, was found for the radium oxidizable species. This may be due to the high ability of the used leaching solutions in step (B.4) to remove the radium species within sludge waste.

This observation confirms the same behavior shown using approach 'A' carried out. Therefore, the oxidizable Ra species is main Ra fraction in waste. Therefore, sequence of the different

Table 1

The individual and actual removal percentages (%) of the different radium species using approach 'A'

Sequence (A.1–A.4)	Leached Ra-species	Removal percentages (%) of Ra-isotopes		
		Ra-226 (1)	Ra-228 (2)	Ra-224 (3)
A.1	Exchangeable	5.7 ± 2.4	6.5 ± 1.4	3.1 ± 0.9
A.2	Acidic	8.9 ± 0.4	7.5 ± 0.9	11.8 ± 0.2
A.3	Reducible	11.9 ± 1.4	18.3 ± 2.5	19.6 ± 0.4
A.4	Oxidizable	51.5 ± 2.1	32.5 ± 4.1	41.9 ± 5.2
Total removal (%)		78 ± 2.8	64.8 ± 4.1	76.4 ± 5.2

(1) Ra-226 determined from the γ -energy line at 186.3 keV (3.29%), (2) Ra-228 determined from the γ -energy line at 911.1 keV (29%), and (3) Ra-224 determined from the γ -energy line at 238.6 keV (45%).

Table 2

The individual and actual removal percentages (%) of the different radium species using approach 'B'

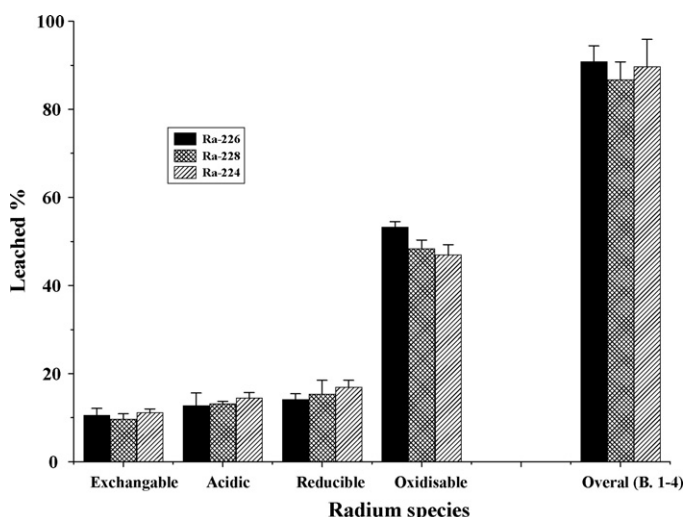
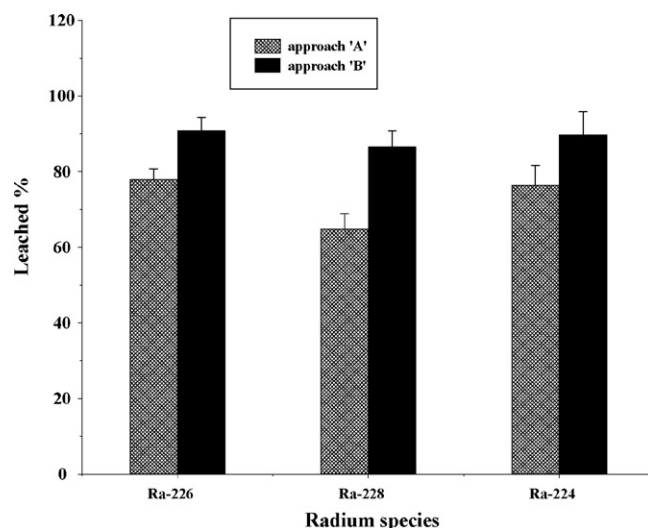
Sequence (B.1–B.4)	Leached Ra-species	Removal percentages (%) of Ra-isotopes		
		Ra-226 (1)	Ra-228 (2)	Ra-224 (3)
B.1	Exchangeable	10.6 ± 1.5	9.7 ± 1.2	11.2 ± 0.8
B.2	Acidic	12.8 ± 2.8	13.2 ± 0.5	14.5 ± 1.2
B.3	Reducible	14.2 ± 1.2	15.4 ± 3.1	17.0 ± 1.5
B.4	Oxidizable	53.3 ± 1.2	48.4 ± 1.9	47.0 ± 2.3
Total removal (%)		90.9 ± 3.5	86.7 ± 4.1	89.7 ± 6.2

(1) Ra-226 determined from the γ -energy line at 186.3 keV (3.29%), (2) Ra-228 determined from the γ -energy line at 911.1 keV (29%), and (3) Ra-224 determined from the γ -energy line at 238.6 keV (45%).

radium species present in the treated waste according to the actual leached percentages (%) can be ordered as

oxidizable > reducible > acidic > exchangeable.

The overall removal percentages (%) of the radium species using the both approaches (A and B) are presented in Fig. 5. It is showed that the overall removal percentages of Ra-226 and Ra-224 are approximately the same when the waste is leached using approaches A and B. It is found that values of the overall removal % of Ra-226 and Ra-224 leached using solutions of approach A are 78 and 76%, respectively. The overall removal % using solutions of approaches is increased to ~90% for Ra-226 and Ra-224 (Fig. 5). On the other hand, the overall leached % of Ra-228 is low comparable to Ra-226 and Ra-224 at the same leaching conditions. The obtained overall removal percentages of Ra-228 are ~65 and 87.5% using solutions of the approaches A and B, respectively (Fig. 5). The variation in the overall removal % between the leached Ra species

**Fig. 4.** Distribution of radium species in TENORM sludge using approach 'B'.**Fig. 5.** Overall removal percentages (%) of radium species leached from TENORM waste sludge using approaches A and B.

from the TENORM sludge waste under the same leaching conditions is difficult to be explained. Finally, treatment of the sludge waste using solutions approach B is relatively efficient compared to approach A, towards the overall removal percentages of Ra species.

4. Conclusion

This paper describes the development of the treatment of a solid TENORM waste produced from the petroleum industry, using selective leaching solutions based on two approaches 'A' and 'B'. The results obtained showed that treatment of the waste through main four successive leaching steps removed ~78 and 91% of Ra-226, 65 and 87% of Ra-228 as well as 76 and ~90% of Ra-224 using approaches A and B, respectively. It is also found that the oxidizable radium species was the main phase present in the waste. The individual removal percentages showed the different radium species in

the waste can be ordered as

oxidizable > reducible > acidic > exchangeable.

The high leached % of Ra species as oxidizable may be due to the high strength of the used solutions (in step A.4 or B.4) to remove Ra species within the sludge waste. It is concluded that the treatment of TENORM wastes using approach B using selective chemical solutions is suitable and efficient to reduce the high activity concentrations of Ra present a different radium species to below the exemption levels recommended by IAEA [1]. It is clear that the obtained results can be used to predict appropriate condition for the further, safe storage of such a waste or their impact on surrounding environment.

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