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Overview about Different Approaches of Chemical Treatment of NORM and TE-NORM Produced from Oil Exploitation

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Additional information is available at the end of the chapter

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Abstract

Crude oil or gas is considered the most important sources of natural radionuclides from the uranium and thorium series. The radionuclides of primary concern to the oil and gas industry are Ra226 (U238 decay) and Ra228 (Th232 decay) due to their radiotoxicity and relatively long half-lives (1620 and 5.75 years, respectively). One of the decay products of U238 is Rn222, a radioactive noble gas. Radon emanates from the ground where it can be breathed in. Radon also decays to alpha-emitting progeny nuclides, so inhaling a single radon atom can lead, ultimately, to up to four alpha decays in the lungs before reaching stability. Alpha particles are considered as internally hazardous if a radioactive source emitting its particles is inhaled or ingested. So, in this chapter we shall make an overview about different approaches of chemical treatment of NORM and TE-NORM produced from oil exploitation.

Keywords: Chemical Treatment / NORM , TE-NORM/ Oil Exploitation / Scales / Sludge

1. Introduction

Most of the natural radionuclides in wastes from crude oil exploitation were firstly discovered in the beginning of the last century. More types of industries have been identified dealing with

materials containing enhanced levels of natural radionuclides, which are summarized as TE-NORM (technologically enhanced naturally occurring radioactive materials). Naturally occurring radionuclides are present at varying concentrations in the Earth's crust and can be concentrated and enhanced by processes associated with the recovery of oil and gas. This "enhanced" NORM, often known as TE-NORM, can be created as a result of industrial processes and human activity, and in addition, can be the by-product of oil, gas production. One of the important examples that can contain elevated levels of NORM, and the radioactive materials may migrate from site to site as the materials and equipment are reused are sludge, pipe scales, produced water, and drilling mud.

Transportation or decay of radioactive elements produces other radionuclides (daughters) from the reservoir to the surface with the produced oil and gas carried out under certain conditions dependent upon pressure, temperature, acidity. NORM with the oil, gas, and water mixture migrate and accumulate in scale, sludge, and scrapings during the production process. Moreover, they form a thin film on the interior surfaces of gas-processing vessels and equipment. The geological formation is considered as important parameters at determining the level of NORM and it was found that the accumulation can vary from one site to another depending on it.

There are three types of radiation emitted by NORM, namely:

· Alpha (α) · Beta (β) · Gamma (γ)

Alpha particles are considered as internally hazardous if a radioactive source of alpha-emitting particles is inhaled or ingested. While beta particles have one (negative) charge and interact more slowly with the material, they are effectively stopped by thin layers of metal, wood, or plastic and considered hazardous only if a beta-emitter source is ingested or inhaled. Gamma emitters are associated with alpha, beta decay with high-energy electromagnetic radiation that interacts lightly with matter. Gamma rays are best shielded by thick layers of lead or other dense materials and are considered as an external hazard to human bodies. Figure 1 details the origins of NORM in the recovery process [1].

2. Natural Radionuclides in the Oil Industry

2.1. Radon

One of the decay products of U238 is Rn222, a radioactive noble gas. Radon emanates from the ground where it can be breathed in. Radon also decays to alpha-emitting progeny nuclides, so inhaling a single radon atom can lead, ultimately, to up to four alpha decays in the lungs before reaching stability. Since radon comes from the decay of geologic uranium, radon concentrations will vary according to local geology. In general, radon dose will be higher in areas that are underground, poorly ventilated, and in areas with high levels of uranium in the rocks.

Crude oil or gas is considered the most important sources of natural radionuclides from the uranium and thorium series. The radionuclides of primary concern to the oil and gas industry

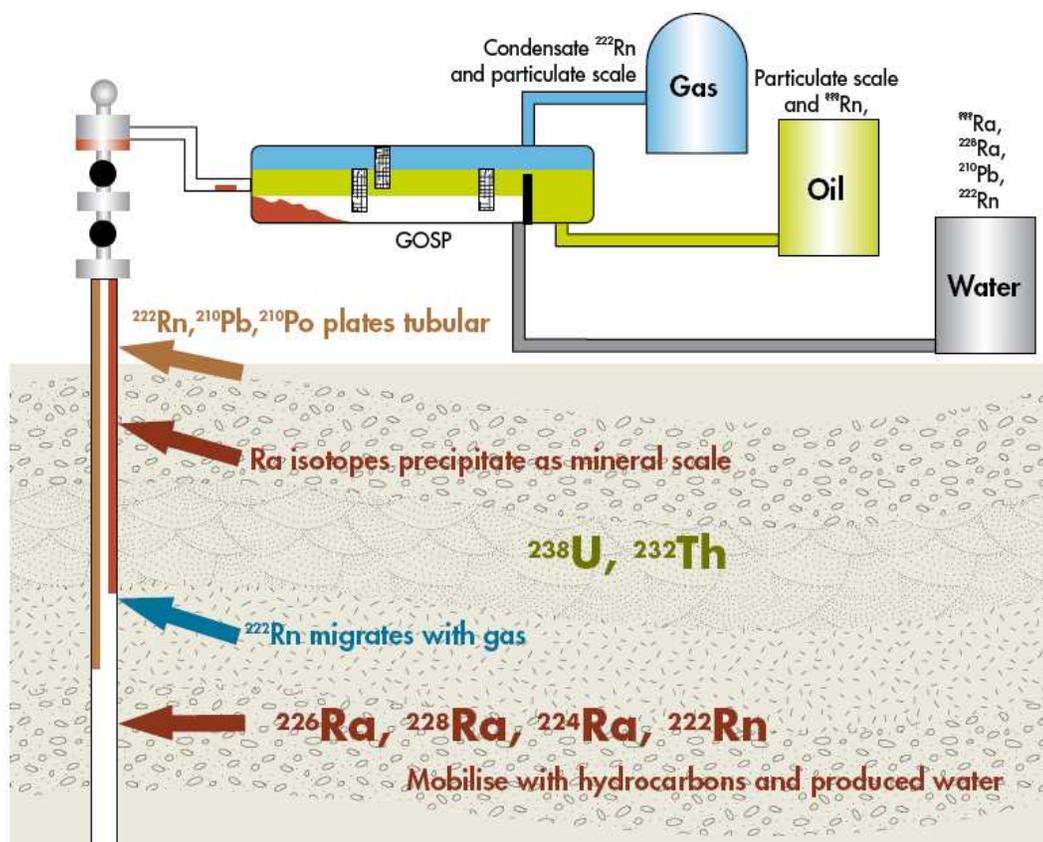


Figure 1. The origins of NORM in the recovery process [1]

are Ra226 (U238 decay) and Ra228 (Th232 decay) due to their radiotoxicity and relatively long half-lives (1620 and 5.75 years, respectively) as shown in Figures 2 and 3 [1]. Radon radionuclides escaping from the adjacent geological formations are soluble in crude oil, but due to its half-life (3.825 days) only Rn222 is

present in the pumped oil in varying concentrations from 10 to 800 Bq/kg [1]. Many previous data on the distribution of the main radon nuclide Rn222 in different gas fields and processing plants were collected in the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) report [2]. Crude oil is usually pumped to the surface together with produce water with radon and radium radionuclides while uranium and thorium usually do not go into solution. Various cations such as barium and strontium, with anions such as sulfate, chloride, or the bicarbonate solubility of radon in water is lower, and the level of Rn222 concentrations in the petroleum formation water was found in the range of 18.5 Bq/dm³ [3]. Very low concentrations measured for the U and Th and produced waters were obtained under the reducing conditions. The same result was found with radium nuclides released by alpha from the surrounding minerals or leaching processes usually recovered by sorption, except for saline waters with high concentration of chloride anions [4–5]. Typical ranges or average values of the radium radionuclide concentrations in the formation or produced water from different oil fields, including the recent data, are listed in Table 1.

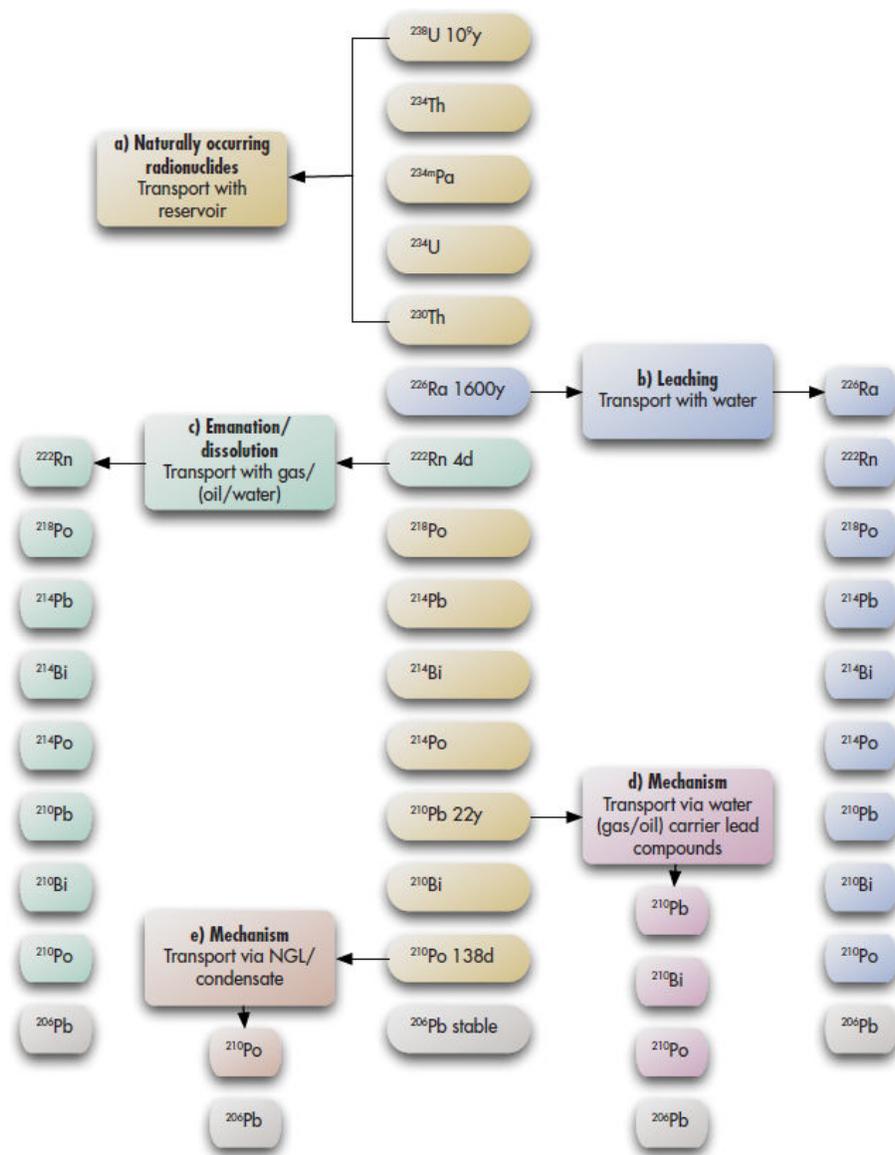


Figure 2. Uranium238 decay series [1]

The worldwide average concentration of these radionuclides in produced water discharged to the environment is estimated at 10 Bq/l. These concentrations are approximately three orders of magnitude higher than the natural concentrations of radium in drinking or sea water.

Scale formation is a complex phenomenon and can be interpreted by the variation of the solubility of carbonates or sulfates or by pressure and temperature changes, water injection into the reservoirs, and evaporation in the gas extraction pipes. Radium and radon concentrations in the pipe scale and waste sludge are dependent on three factors: the amount of Ra present in the subsurface soil, treatment processes applied during oil or gas production, and formation of water components. Most radium radionuclides are efficiently concentrated from the water phase during formation of the scale. Therefore, the measured levels of activity concentrations both in the separated sludge and in the solid scale are much higher than those

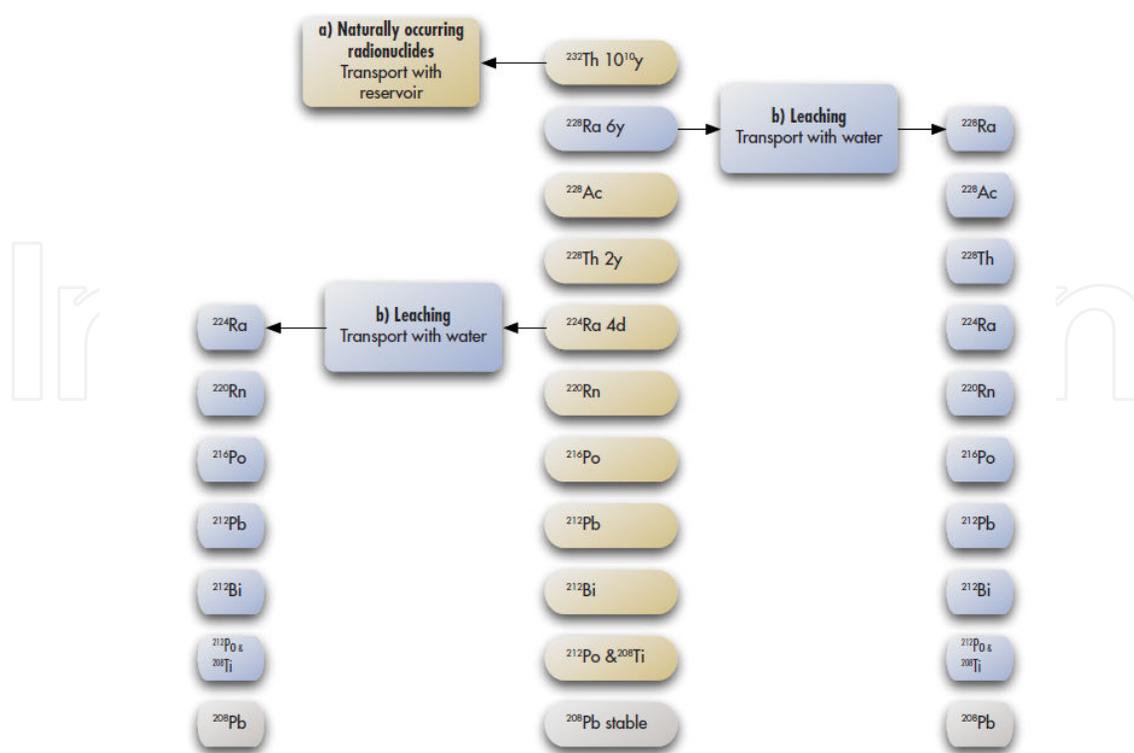


Figure 3. Thorium232 decay series [1]

measured in the produced water from the oil industry. Ra226 and Ra228 activity concentrations measured in the solid scale and sludge are listed in Table 2.

^{228}Ra (Bq/dm ³)	^{226}Ra (Bq/dm ³)	Sample	Field
	1000–950.000	Scale	Algeria [8]
	21.000–250.000	Scale	Australia [9]
	19.100–323.000	Scale	Brazil [20]
48.000–300.000	121.000–3.500.000	Scale	Brazil [21]
4210–235.000	77.900–2.110.000	Scale	Brazil [22]
148.000–2.195.000	97–151	Scale	Congo [11]
101.500–1.550.000	68.900	Scale	Egypt [23]
24.000	7541–143.262	Scale	Egypt [12]
35.460–368.654	< 2.7–2890	Scale	Italy [11]
200–10.000	510–51.000	Scale	Kazakhstan [24]
130.120–206.630	114.300–187.750	Scale	Malaysia [25]
300–33.500	300–32.300	Scale	Norway [26]
30.000	.08–1.5	Scale	Saudi Arabia [27]
	31–1189	Scale	Tunisia [11]
	4300–658.000	Scale	Tunisia [28]
	1000–1.000.000	Scale	UK [29]
	up to 3.700.000	Scale	USA [30]

^{228}Ra (Bq/dm ³)	^{226}Ra (Bq/dm ³)	Sample	Field
	5.1–14.8	Formation water	Algeria [7–8]
23 ^a	17 ^a	Produced water	Australia [9]
0.05–12	0.01–6	Produced water	Brazil [10]
1–59	5.1 ^a	Produced water	Congo [11]
-	5–40	Formation water	Egypt [12]
2.8 ^a	0.2–2	Produced water	Italy [11]
0.5–21	0.3–10.4	Formation water	Norway [12]
8.8–60.4	3.3 ^a	Produced water	Norway [13]
-	0.5–16	Produced water	Norway [14]
-	9.9–111.2	Produced water	Syria [15]
0.7–1.7	1.7 ^a	Produced water	UK [16]
15.1 ^a	0.1–60	Produced water	USA [6]
25–30	0.15–21.6	Produced water	USA [17]
	12.6 ^a	Oilfield brine	USA [18]
	22–30	Produced water	USA [19]

a: Mean activity concentration.

Table 1. Ranges of activity levels in produced water from the oil fields

^{228}Ra (Bq/dm ³)	^{226}Ra (Bq/dm ³)	Sample	Field
	15.400–76.100	Scale	USA [31]
	25.000	Sludge	Australia [9]

Table 2. Ranges of activity levels of ^{226}Ra in different scale and sludge samples

From the data obtained in Table 2, it was found that the concentration levels of radium nuclides in sludge were much lower than those of the scale. Environmental Protection Agency (EPA) estimated the average radium nuclide concentration to be around 2800 Bq/kg and 18,000 Bq/kg in sludge and scale, respectively [32]. The exposure is caused by external radiation coming from the ^{226}Ra radionuclide and its progenies: $\text{Pb}214$ and $\text{Bi}214$ as well as by inhalation of α -emitting radionuclides; $\text{Rn}222$ as well as $\text{Po}218$ and $\text{Po}214$ formed from $\text{Rn}222$ escaping into the air adjacent to scale deposits, see Table 3.

The main types of scales encountered in oil and gas facilities are sulfate scale such as BaSO_4 , which is called barite. Colorless or milky white is the common one, but can have any color, depending on the impurities trapped in the crystals during barite formation. The high density of barite is responsible for its value in many applications. It is always chemically inert and

Reported range ($\mu\text{Sv/h}$)	Country
Background–100	Algeria [8]
10–300	United Kingdom [8]
50–100	Egypt [23]
0.1–6	Congo, Italy, Tunisia [11]
up to 300	USA [5]

Table 3. Exposure rate levels in the oil industry

insoluble. Due to the high chemical similarity of radium with barium (Ba), strontium (Sr), and calcium (Ca), radium co-precipitates with Sr, Ba, or Ca scale forming radium sulfate, radium carbonate, and in some cases radium silicate is produced. As mentioned before, the mixing of seawater, which is rich in sulfate, with the produced water, which is rich in Cl^{-1} , increases the scaling tendency. In addition, any change in pressure and temperature or acidity of the formation water contributes to scale build-up. The build-up of scale on the interior of a pipe is shown in Figure 4. The activity concentrations of Ra226 and Ra228 in hard scales in Egypt and some other countries were mentioned in Table 4.



Figure 4. The build-up of scale on the interior of a pipe

Inhibitors may be applied to the piping complexes to prevent scales from slowing the oil extraction process. If the scales contain TE-NORM, the radiation will remain in solution and eventually be passed on to the produced waters. The United States generated annually around 100 tons of scale per oil well. Sometimes, in some cases brine is introduced into the produced water to enhance the recovery of radium; this also increases scale formation.

Country/region	Activity (Bq/g)		Ref.
	²²⁶ Ra	²²⁸ Ra	
Egypt/oil field			
Abu Rudeis	68.9	24	[33]
Gabal El Zeit	14.8	4.3	[34]
Badr El Din	31.4	43.3	[34]
Red Sea	195	897.8	[35]
Western desert	59.2	244.5	[35]
Other countries			
Australia	20–70		[36]
USA	70.8		[37]
Algeria	1–950		[38]
Tunisia	4.3–658		[39]
UK	1–1000		[40]

Table 4. Activity of ²²⁶Ra (U-series), ²²⁸Ra (U-series), and ⁴⁰K in the TE-NORM in Egypt and some countries

2.2. NORM in sludge

Radioactive molecules containing radium which were not incorporated into scale can be found in sludge, produced sands, and produced waters. Before the treatment investigations, the activity concentrations of the main three radium isotopes were measured in sludge [41]. It is found that the average activity level of Ra226, Ra228, and Ra224 for samples taken from Abu Rudeis region, Government of Sinai–Egypt, were 11950, 1750, and 1900 Bq/kg, respectively. Due to the accumulated TE-NORM wastes in huge amounts and release of high activity concentrations to the environment and the workers, treatment approaches are suggested to reduce the human and environmental hazard potential. Sludge is composed of dissolved solids which precipitate from produced water as its temperature and pressure change. Sludge generally consists of oily, loose material often containing silica compounds, but may also contain large amounts of barium.

2.3. NORM in natural gas

Radon is a radioactive noble gas, present in varying level in natural gas in oil and gas formations. In the absence of natural gas, radon easily dissolves in the light hydrocarbon. Radon usually follows the gas stream when produced with the oil and gas. If the natural gas is fractionated, higher percentage of radon can concentrate in the propane streams and lower degree in the ethane streams. Most of the radon decay products are found in ambient aerosols, airborne particulates, or surfaces. Most radon progeny are short-lived, with the exception of Po210 and Pb210, which have relatively long half-lives of 138 days and 22.6 years, respectively. Formation of thin radioactive films on the inner surfaces of gas-processing equipments, such

as scrubbers, compressors, reflux pumps, control valves, and product lines, due to the release of daughters of radon.

2.4. NORM in produced water

Formation water at oil and gas reservoirs called produced water float to the surface during oil and gas production. However, gas reservoirs typically produce smaller quantities whereas the oil reservoirs can contain large volumes of formation water. Water is injected into the reservoir to maintain pressure and or maximize production in most fields. The produced water stream can be one of the largest waste products, by volume produced from oil and gas industry. It was found that the produced water contains a complex mixture of inorganic compounds, such as dissolved salts, trace metals, suspended particles and organic compounds such as dispersed and dissolved hydrocarbons, organic acids, and residual chemical additives such as scale and corrosion inhibitors that are added into the hydrocarbon production process. Technologies of treatment depending on the application and particular field conditions. Also, it is to consider include combinations of gravity and / or mechanical separation and chemical treatment, and may include a multistage system, typically including a parallel plate separator, followed by a gas flotation cell or hydrocyclone. For disposal of produced water to sea, some criteria should be considered to reduce the volume of produced water, such as:

Select adequate well management during well completion to minimize water production;

Minimize water production by recompletion of high water-producing wells;

To be economically feasible, use down hole fluid separation techniques, where possible.

For reducing environmental hazards related to residual chemical additives in the produced water stream, where surface disposal methods are used, production chemicals should be selected carefully by taking into account their volume, toxicity, and bioaccumulation potential [42]. The average worldwide activity levels of uranium (U), thorium (Th), and potassium (K) [43] and the exemption activity levels of NORM as recommended in the IAEA basic safety standards [44] were given in Tables 5 and 6. The average worldwide levels of the most common radiological indices [43] were given in Table 7. These indices include radium equivalent (Ra_{eq}), total absorbed dose ($D_{\gamma r}$), and effective annual dose rate (EDAR).

Radionuclide	U	Th	K
Activity level (Bq/Kg)	50	50	500

Table 5. The average worldwide activity levels of uranium (U), thorium (Th), and potassium (K)

Radionuclide	U ²³⁸	Ra ²²⁶	Rn ²²²	Th ²³²	Ra ²²⁸	Ra ²²⁴
Exemption level (Bq/g)	1	10	10	1	10	10

Table 6. The exemption activity levels of NORM as recommended in the IAEA basic safety standards

Radiological indices (Unit)	Ra-eq (Bq/Kg)	D _{yr} (nGy/h)	EADR (mSv/yr) for worker	EADR (mSv/yr) for Public
Activity level (Bq/Kg)	370	55	20	1

Table 7. The average worldwide levels of the most common radiological indices

3. Resources of NORM and TE-NORM

Earlier, we saw that many natural materials contain radioactivity. Some of these materials are used in manufacturing: clays and various minerals. In other cases, radioactive elements are used in manufacturing – not because of the radioactivity, but because of other chemical or physical properties. For example, thorium is radioactive, and it has a high melting temperature; for this reason, thorium is used in the manufacture of some welding electrodes, gas lantern mantles, and jet turbine blades. These products and the wastes from their manufacture will contain low levels of radioactivity. Many fossil fuels are associated with radioactivity; the geochemistry of uranium is such that it is often found in petroleum, natural gas, and coal deposits. The equipment used to extract and process these materials is often contaminated with NORM materials, especially with radium, which can be present in the scales and sludges from processing these materials. Although refined petroleum and natural gas products do not contain large levels of these nuclides, coal can; so, fly ash often contains elevated levels of radioactivity as well. In fact, when 90% or more of the coal is burned, all of the radioactivity is left in the remaining 10% that is ash. Thus, fly ash is considerably more radioactive than is the original coal. Uranium and thorium are fairly common in nature, and many minerals contain elevated levels of these radioactive elements and their decay series nuclides. In particular, minerals containing rare earth elements (such as monazite), titanium minerals, niobium ores, and some precious metal ores can be associated with elevated levels of radioactivity. When the minerals are processed, the metal is removed from the ore, and the radioactivity concentration in the remaining waste is even higher than in the original ore. In addition to all of these, anything that contains potassium will be somewhat radioactive because 1/100% of potassium is naturally radioactive. Potassium is found in many minerals, some forms of clay, and in many products – consumer and industrial both – so sometimes these items will also give high levels of radiation. Loads of bananas, kitty litter, and salt substitute all contain enough radioactive potassium to set off radiation alarms.

3.1. NORM and TE-NORM at the landfill

Many industries produce wastes that might contain natural radionuclides, and most of these wastes end up at landfills, either hazardous or otherwise. The majority of TE-NORM sources waste arise from industrial processes. Most of the wastes obtained are produced in very large amounts with low activity. Improper disposal, recycling, and reuse of TE-NORM have led to circumstances resulting in contamination and unnecessary public exposures.

Disposal of TE-NORM in piles or stacks can lead to contamination of groundwater and airborne releases of radioactive particulates and radon. Improper use and/or disposal of the TE-NORM used for soil conditioning or fill around homes can lead to accumulation of radon gas in homes, direct exposure to individuals, and contamination of soil and of the crops growing in the soil. Reuse of TE-NORM-contaminated materials, such as in concrete aggregate, ceramic industry, and red stone can lead to increased radiation risks to members of the public in a variety of ways.

The main radionuclides daughter found in the uranium series in industrial TE-NORM are ^{238}U , ^{234}U , ^{230}Th , ^{226}Ra , and ^{222}Rn , while the thorium series are ^{232}Th , ^{228}Ra , and ^{220}Rn . In addition, ^{40}K should be characterized. Radium226 is used as a monitor to show the relative activity and volume among the TE-NORM sectors. It was found that Radium226 is in equilibrium with its progeny, but Radium228 is not and their activity appears to be about three times greater than Radium228.

4. General Technologies for Treatment of TE-NORM Waste

4.1. Use of reagents

A water-bath heater from a gas production facility in North Sea (e.g., the Netherlands) has been used as a test for equipment in laboratory aimed at the in situ removal of TE-NORM. This is achieved by circulating an aqueous solution of commercially available scale dissolver through the contaminated equipment. For this purpose, some scale dissolvers which are widely used within exploration and production are commonly based on chelating chemistry and reportedly successfully applied in the dissolution of low specific activity scales [45]. For instance, application of scale dissolver reagents resulted in the rapid and complete removal of ^{226}Ra and progeny-containing sulfate scales as well as ^{210}Pb -containing sulfide scales from the head internals. These studies were performed using scale dissolver consisting of 15% v/v acetic acid and 1% v/v strongly oxidant, e.g., KMnO_4 . This reduced the total activity from 20 Bq/cm² to 6 Bq/cm², the residual activity may be removed using 0.5 M citric acid. Also, scale dissolver solution containing 15% v/v acetic acid plus 1% v/v hydrogen peroxide was used to dissolve TE-NORM contaminated by overall activities of 2000 Bq (^{226}Ra)/g and 600 Bq (^{210}Pb)/g. This was followed by water flush. Generally, the application of a chemical scale dissolver can remove 95–99% of TE-NORM present in exploration and production facilities. On the other hand, radioactive scales containing ^{226}Ra and its progeny, such as barium sulfate scales, are removed chemically using hydrochloric acid, and the dead acid is disposed as waste after appropriate radiometric checks [46].

4.2. Recycling equipment

The contamination produced from the accumulation of toxic materials mainly include heavy metals such as mercury and radioactive materials of the natural origin (e.g., ^{226}Ra , ^{228}Ra , ^{210}Pb). For decontamination purpose, the contaminated equipments were taken into melting plant, especially built for this process; its annual capacity is 2000 tones of steel and metal scrap

contaminated with mercury and TE-NORM. After melting, the radiological measurements showed that the produced metal did not contain any detectable residual of TE-NORM, and can be re-used again in steel works. About 98% of TE-NORM were bound to the slag and ~2% were detected in the filter dust, mainly consisting of the nuclides ^{210}Pb and ^{210}Po . The secondary waste produced is ~43% of the total weight of the material supplied, whereas TE-NORM waste consists of ~95% of slag and ~5% coarse dust [45].

Chemical separation of the radionuclides incorporated in the contaminated equipment (pipelines, tubes, pumps) is carried out by melting at 1400°C , to further fractionation of radionuclides in melt, slag, or dust. The analysis of data showed that most of ^{238}U and ^{232}Th series are transferred from melt (dense main component, contains only 1% of the remainder radioactivity) into the slag (light minor component, contains only 98% of the total radioactivity). All activity of ^{210}Pb was concentrated in the filter dust, because it is evaporated at normal melting temperature above 1300°C [47]. Equipment should be decontaminated to less than 0.4 Bq/cm^2 for alpha emitters or 4 Bq/cm^2 for beta and gamma emitter, before any release.

4.3. Solid TE-NORM waste

For TE-NORM-contaminated scale, sludge, and soils with very low levels of radioactivity, a suitable disposal option is to spread over the ground and mix with non contaminated soils, to dilute the contaminated soils and reduce the radioactivity level to background levels. This type of disposal is often the most cost-effective [48]. Subsurface disposal options include underground injection and down hole encapsulation. This type of disposal is widely acknowledged as one of the most environmentally sound methods of disposing TE-NORM-contaminated sludge. The two common forms of subsurface disposal are:

- i. Underground injection, established by mixing a TE-NORM-contaminated waste with cement in a slurry, then injecting the formed mixture into a deep subsurface formation.
- ii. Down hole encapsulation, entails placing TE-NORM-contaminated scale, sludge, tubes, and other small pieces of the production equipment (e.g., valves, filters, pumps, screens) inside the casing of a well, which is to be plugged with cement and then abandoned.

4.4. Liquid TE-NORM waste

TE-NORM in slurry form (e.g., waste water or solids mixed with water) can be re-injected into deep formations for disposal [18]. There are three classes for injection:

Class (I): This option is used for any liquid TE-NORM wastes. Over 90% of all produced water resulting from oil and gas operations is injected through wells into permeable disposal formations, which lie below underground sources of drinking water (USDW), and surrounded by impermeable layers. After injection, the well is closed, sealed with cement, and capped, effectively isolating injected materials from the surface. Injection costs vary based on volume, depth, formation pressure and permeability, and other factors. The cost of injecting a slurry could be comparable, or slightly higher.

Class (II): Well injection, when TE-NORM concentrations prevent disposal in class (I). The used wells in this class are deeper and are constructed to give great protection against potential migration of injected fluids to (USDW). Disposal in class (II) well is to some degree more expensive than class (I) injection. Also, transportation costs would be higher, as limited number of class (II) disposal wells exist.

Class (III): Deep well injection, these wells consist of injecting liquid wastes contaminated by TE-NORM fluids into the well at sufficiently high pressure to create a fracture in permeable shale formations. After the scale/water mixture is displaced into the fracture, then the pressure is reduced, and the fracture closes.

The scale is trapped between the fracture wells and is incapable of re-entering the well bore. Deep well injection is generally regarded as an effective method for the disposal of TE-NORM waste because it does not depend on the mechanical integrity of the well to prevent potential subsurface contamination.

When the radium ions are present in the produced water, any drops in pressure and temperature can lead to the solubility products of their sulfates and carbonates being exceeded. This is the main cause for precipitation of radium as sulfate and carbonate scales on the inner walls of production tubules, well heads, valves, pumps, separators, water treatment vessels, gas treatment and oil storage tanks. Particles of clay or sand co-produced from the reservoir may also act as catalytic surfaces for initiating scale deposition or may adsorb the cations. Daifullah and Awwad [49] found that oil shale is a good adsorbent for Hg(II) from aqueous solution. Shales normally contain at least 35% clay minerals, and a significant fraction contains potassium as an essential constituent. Removal of mercury (II) from wastewater was studied using camel bone charcoal [50]. Shales can adsorb the series radionuclides [51]. Common anthropogenic sources of mercury include nuclear fuel production as part of the uranium purification and isotope separation process (^{235}U and ^{238}U). Mercury in the form of Hg(II) also enters aquatic environments from industrial and nuclear fuel wastes. The feasibility of using oil shale for removal of Hg(II) has been addressed. Also, it was found when using seawater to enhance oil recovery, it will increase the sulfate concentration of the produced water and enhance scale deposition. So, new trends should be used to solve these problems.

5. New Approaches Used in the Treatment of NORM and TE-NORM Produced from Sludge Waste Obtained from Oil and Gas Production

In oil and gas production, the TE-NORM may be solid waste as scale and/or sludge and produced water. Our literature shows that TE-NORM contains activity concentrations of Ra226 ranging from undetectable levels to 1000 kBq/kg [52] and the activity level concentrations of Ra226 in TE-NORM can be much higher than the exemption levels established by IAEA [53]. As mentioned before, the recommended exemption level for uranium-series is: U238 = 1 Bq/g and Ra226 = 10 Bq/g. For thorium decay, a chain is: Th232 = 1 Bq/g, Ra228 = 10 Bq/g, and Ra224 = 10 Bq/g.

It is important to focus on the environmental and health impacts from the uncontrolled release of TE-NORM wastes [54, 34, 23]. 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 (Rn222) decayed from radium, and/or ingestion of waste dust during the periodical maintenance of the equipment used. Treatment of TE-NORM wastes from many industries still needs more efforts. The traditional methods used before include subsurface disposal, volume reduction, use of scale and/or sludge inhibitors, recycling, and leaching using chemical solutions [55–57]. In addition, a simple extraction process is carried out using saline solutions and chemical solutions [41, 58] to removal of Ra226, Pb210, Rn220, Th232, Ra228, and Ra224 from TE-NORM wastes produced from oil and gas industry.

Sequential chemical treatment for radium in sludge or scale to reduce its activity concentration in oil and natural gas production fields is recommended. The proposed treatment method was carried out on the basis of two approaches using chemical solutions through four successive steps.

Successive four steps were used to leachate the radium species in the waste of TE-NORM [59].

Before the treatment investigations, the activity concentrations of the main three radium isotopes were measured. It is found that the average activity level of Ra226, Ra228, and Ra224 were 11950 ± 1700 , 1750 ± 200 , and 1900 ± 250 Bq/kg, respectively. Due to the high accumulation of radium species in huge amounts and high activity concentrations causing health hazards to the environment and the workers, sequential chemicals treatment approaches are suggested as a new trend to reduce the human and environmental hazard potential.

5.1. Approach of treatment

It is well known that the environmental behavior and toxicity of trace elements and radionuclides depend strongly on their physicochemical forms (i.e., speciation) in the environment [60]. In this study, the applied treatments involve four steps achieved sequentially for each approach. Selective extraction of the different radium species present in TE-NORM waste, such as water-soluble species, exchangeable, carbonates, reducible species, oxidizable organics becomes allowed.

5.1.1. Approach 1

The treatment of the radium content in TE-NORM using sequential chemical leaching was based on the individual extraction for each Ra species in the waste, according to the successive four steps (A.1–4). From the data obtained, it was found that the exchangeable radium species was removed from the waste. The removal percentages (%) for Ra226, Ra228, and Ra224 are 5.7 ± 2.4 , 6.5 ± 1.4 , and $3.1 \pm 0.9\%$, respectively. These values are high if comparable to the exchangeable Ra species present in and extracted from phosphate ores [61].

In the second step of leaching (A.2), the data obtained 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 Ra226, Ra228, and Ra224, respectively. This leached part is related to the Ra fraction bounded to carbonate species (acidic fraction of

species Ra). In step number three (A.3), it was found that the removal percentages of Ra226, Ra228, and Ra224 are 10.9 ± 1.4 , 18.3 ± 2.5 , and $19.6 \pm 0.4\%$, respectively. This leached part is related to radium species bounded to metal-oxides such as the Fe-Mn-oxides [62]. The remaining part of radium species found bounded to organic matter and sulfides was leached through two substeps (A.4). The final removal percentages by this approach related to Ra226, Ra228, and Ra224 are 51.5 ± 2.1 , 32.5 ± 4.1 , and $41.9 \pm 5.2\%$, respectively, as shown in Figure 5.

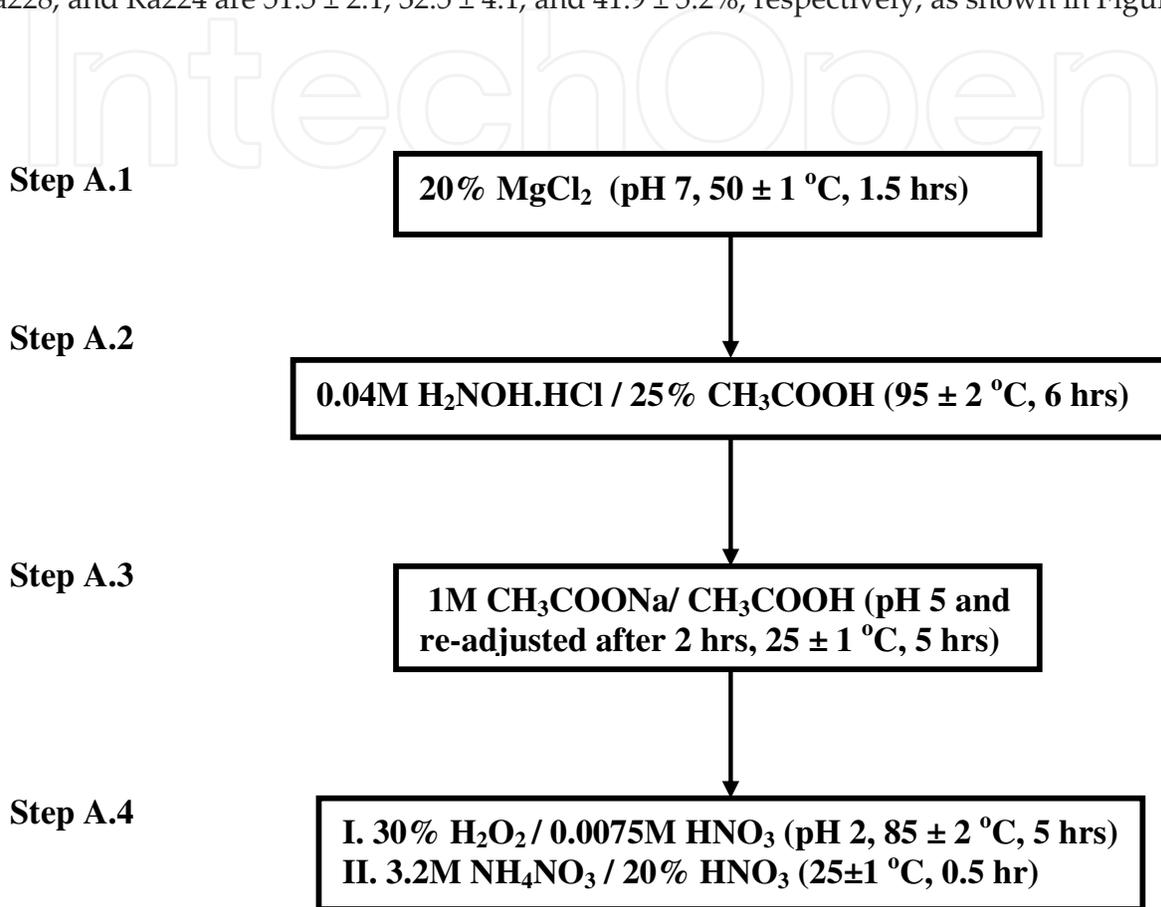


Figure 5. Sequential leaching of the radium content in TE-NORM was based on the individual extraction for each Ra species in the waste

According to approach 1, the successive leaching steps released most of the radium species found in the treated TE-NORM waste. Also, from the data obtained, it is observed that the real removal percentages (%) of Ra226, Ra228, and Ra224 are 78 ± 2.8 , 64.8 ± 4.1 , and $76.4 \pm 5.2\%$, respectively. There is variation in the leaching % for each Ra-isotope due to the radiochemical factors such as the differences in their half-lives. Figure 6 shows the leaching 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 concentration of leaching solutions used to remove Ra species within the TE-NORM sludge waste. Therefore, the radium species in the treated waste using approach A can be ordered as: oxidizable > reducible > acidic > exchangeable.

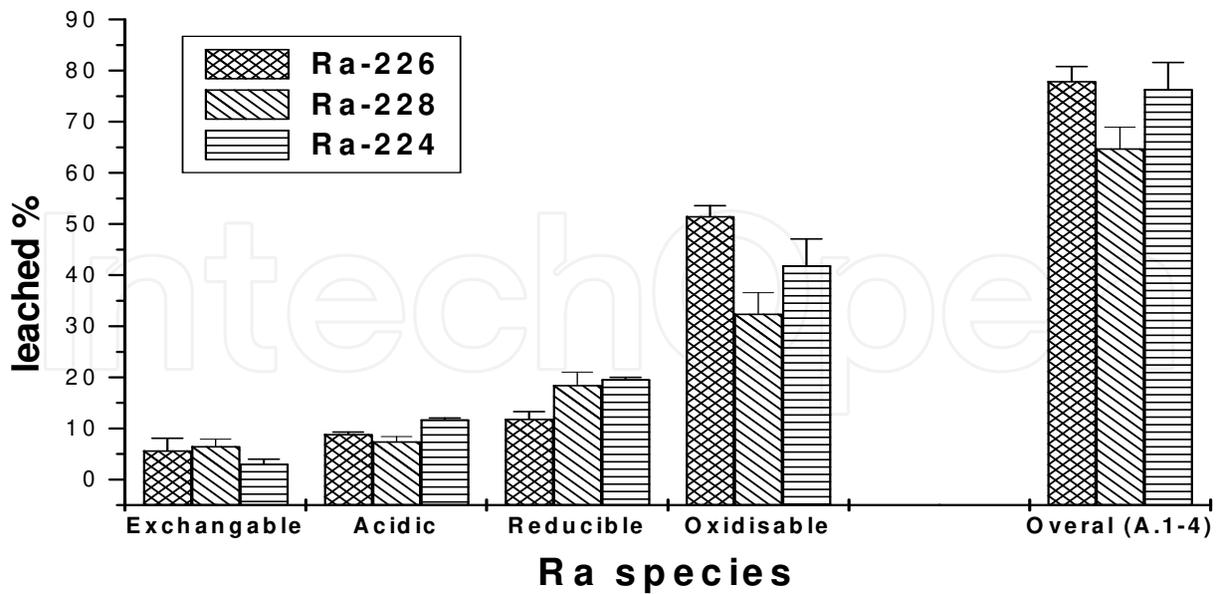


Figure 6. Distribution of radium species in TE NORM ludge using approach A

5.1.2. Approach 2

In approach 2, the TE-NORM waste was treated sequentially using different chemical leaching, through four leaching steps. The de-aerated and de-ionized H_2O (pH 6.7, $25 \pm 1^\circ C$, 4 h), 1M CH_3COONH_4 (pH 6.8, $25 \pm 1^\circ C$, 4 h) as water-soluble and exchangeable solutions for removal of Ra species are used. The results showed that the leached percentages (%) of radium isotopes are 10.6 ± 1.5 , 9.7 ± 1.2 , and 11.2 ± 0.8 % for Ra226, Ra228, and Ra224, respectively (step B.1).

In the second leaching process (B.2), the acidic radium species such as carbonates, and in addition, some iron and manganese oxides are removed. The leaching percentages (%) of radium species are 12.8 ± 2.8 , 15.2 ± 0.5 , and 16.5 ± 1.2 % for Ra226, Ra228, and Ra224, respectively. The remaining waste was leached through two successive substeps. The solutions used are selective to the reducible radium species in the waste, such as manganese oxides, amorphous iron oxide, and moderately reducible phase (step B.3). The obtained removal percentages (%) of Ra226, Ra228, and Ra224 are 14.2 ± 1.2 , 17.4 ± 3.1 , and 19.0 ± 1.5 %, respectively. Finally, the remaining 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 ± 2.3 % for Ra226, Ra228, and Ra224, respectively, as shown in Figure 7.

From the data obtained from two leaching sequence mentioned above, it was found that using selective chemical solutions is more efficient when dealing with the different radium species present in the TE-NORM waste. Also, the data showed that the overall removal percentages (%) of all radium species are 90.9 ± 3.5 , 86.7 ± 4.1 , and 89.7 ± 6.2 % for Ra226, Ra228, and Ra224, respectively. These values indicate that the amounts leached of the three radium isotopes by this approach are nearly the same. Figure 8 represents distribution of the actual removed (%)

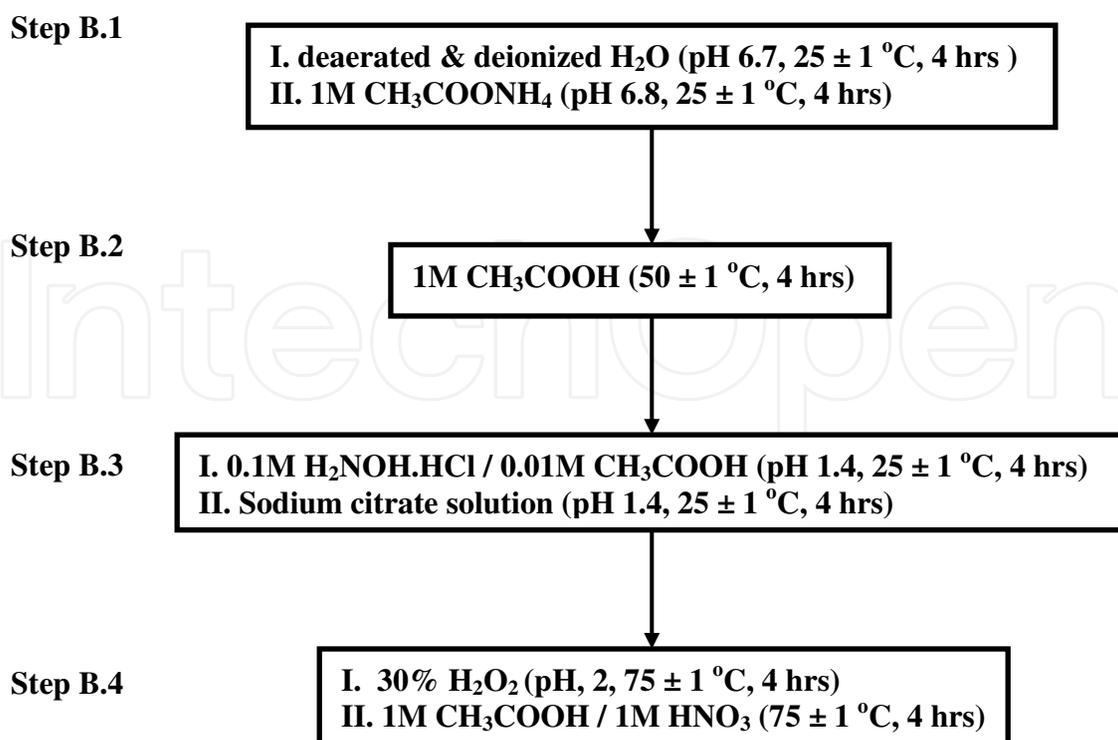


Figure 7. Sequential leaching of the radium content in TE-NORM was based on the individual extraction for each Ra species in the waste

toward different types of the radium species found in the treated TE-NORM waste. It is found that the high removal % of Ra226 is obtained for the radium oxidizable species. This is due to the high ability of the leaching solutions used in step (B.4) to remove the radium species from sludge waste. This conclusion confirms that the same behavior is obtained when using approach A. Therefore, the oxidizable Ra species is the main Ra fraction in waste. So, the net conclusion, the sequence of the different radium species present in the treated waste by leaching (%) can be ordered as: oxidizable > reducible > acidic > exchangeable as shown in Figure 8.

The overall removal (%) of the radium species using the both approaches (A and B) are illustrated in Figure 9. It is showed that the overall removal percentages of Ra226 and Ra224 are nearly the same when the waste is leached using approaches A and B. It is found that values of the overall removal % of Ra226 and Ra224 leached using solutions of approach A are 78% and 76%, respectively. On the other hand, it was found that the overall removal % using solutions of approach B is increased to ~90 % for Ra226 and Ra224. While the overall leached % of Ra228 is low comparable to Ra226 and Ra224 at the same leaching conditions, the obtained overall removal percentages of Ra228 are ~65% and 87.5% using solutions of the approaches A and B, respectively (Figure 9). The variation in the overall removal % between the leached Ra species from the TE-NORM sludge waste under the same leaching conditions is difficult to be explained. Finally, treatment of the sludge waste using solutions of approach B is more efficient compared to approach A, toward the overall removal percentages of Ra species.

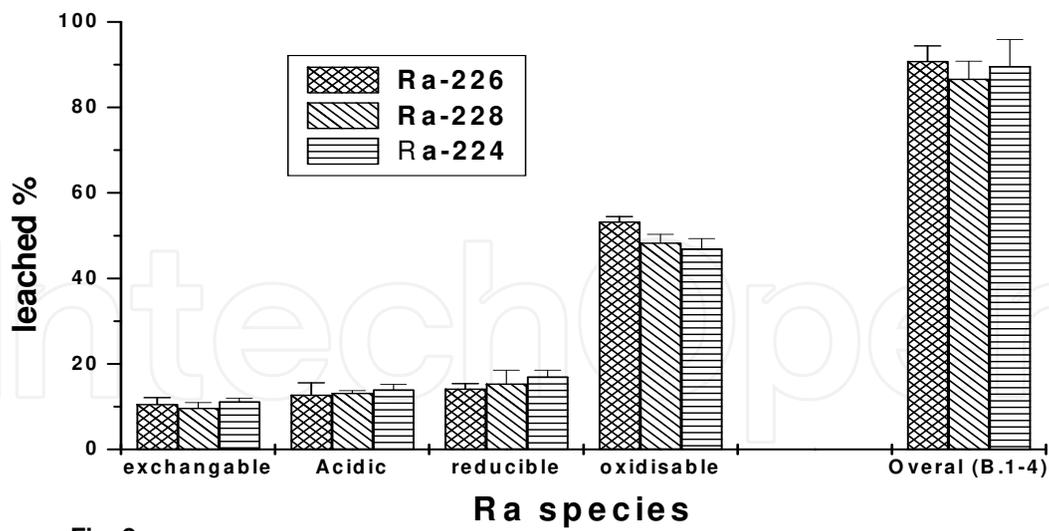


Figure 8. Distribution of radium species in TENORM sludge using approach B

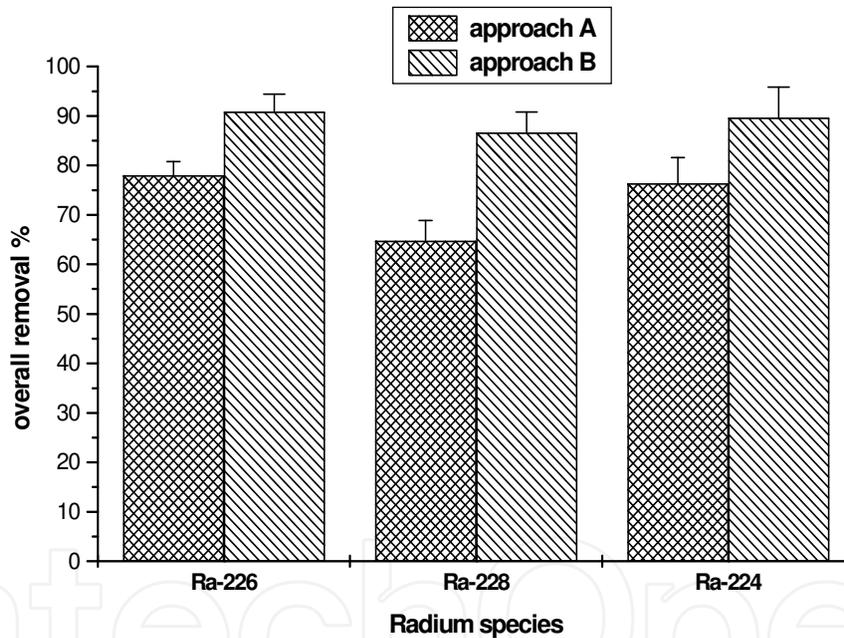


Figure 9. Overall removal percentages (%) of radium species leached from TENORM waste sludge using approaches A and B

The sequential chemical treatment could be the key point for environmental-friendly leaching for TE-NORM waste to select the suitable chemicals for the treatment processes [33].

The other alternative process for treatment of these wastes is leaching or solubilization of the different radionuclides. This is based on partial dissolution of the radionuclides using strong acids or by conversion of hardly or insoluble radionuclides forms to easily soluble salts. Within these merits, investigations were carried out to assess the direct leaching of radionuclides by HCl or HNO₃ or by treating the waste with carbonate solutions followed by leaching the

formed carbonates with dilute acid solution. The different conditions for the maximum removal of the radionuclides Pb210, Ra226, and Ra228 from the sludge and the scale wastes are given. From this table, it is clear that leaching with nitric acid produced better leaching efficiency for the removal of Pb210, Ra226, and Ra228 and then the use of hydrochloric acid. This is relating mainly to the oxidizing action of nitric acid. It is also clear that treatment with carbonate before leaching adds some benefits to the removal efficiency. This can be related to the possible conversion of the sulfate salts to the carbonate, which is easily leachable by dilute acids.

Leaching the carbonate treated sludge and scale wastes by high acid concentration can produce better removal for the different radionuclides, Table 8, yet use of strong acid is not recommended for its hazardous action. Therefore, and out of the different leaching systems studied, it can be recommended that the treatment of both the sludge and the scale wastes by 10% Na₂CO₃ followed by leaching with 1 M HNO₃ solution is recommended. This treatment will remove more than 70% of Pb210, Ra226, and Ra228 from scale waste and more than 55% of the same radionuclides from the sludge waste. It is also noted that the % removal of Ra226 is different than that of Ra228. This suggests that Ra226 is concentrated in different species of these wastes [63].

Method	Removal, %					
	Pb210		Ra226		Ra228	
	Sludge	Scale	Sludge	Scale	Sludge	Scale
HCl (7.5M)	36±2.1	56±2.8	29±1.5	19±1	22±1.2	34±1.7
10%Na ₂ CO ₃ /0.5M HCl	63±3.1	77±3.8	52±2.8	50±2.5	39±2	56±2.8
10%(NH ₄) ₂ CO ₃ /0.5MHCl	21±1.1	63±3.1	23±1.1	32±1.8	44±2.2	37±1.8
25%(NH ₄) ₂ CO ₃ /0.5MHCl	55±2.6	50±2.5	56±2.8	8.5±0.4	66±3.3	44±2.1
10%Na ₂ CO ₃ /1M HCl	66±3.5	76±3.7	54±2.6	53±2.6	47±2.7	85±4.3
(NH ₄) ₂ CO ₃ /1M HCl	56±2.6	67±3.4	58±2.7	48±2.4	68±4.1	63±3.2
HNO ₃ (7.5M)	37±2.2	53±2.5	35±2	16±0.8	21±1	37±1.8
10%Na ₂ CO ₃ /1M HNO ₃	67±3.5	72±3.7	76±4.3	74±3.7	55±2.6	83±4.2
(NH ₄) ₂ CO ₃ /1M HNO ₃	65±4	71±3.6	55±2.9	42±2.1	47±2.3	48±2.4

Table 8. Comparison of maximum % removal of environmental interest radionuclides by different methods

Now, interesting study was done by our team using the solvent extraction technique for treatment of TE-NORM at scales on the interior of a pipe used in exploration of gas and oil industry, and several parameters were studied, such as the effect of contact time, organic extractants concentration, organic liquid/solid ratio, temperature, effect of different aliphatic and organic diluents. From the data available up till now, it can be concluded that kerosene as a diluent has a good efficiency on the E % of the radionuclides with the different organic

extractants used. The extraction percent order with different types of organic extractants for ^{226}Ra , separation of ^{228}Ra , ^{238}U , ^{210}Pb , and ^{40}K at kerosene was found in the following order:

TOPO \approx TBP > TBPO > DEHPA > TPPO > TPAsO for ^{226}Ra

TBP > TOPO > DEHPA > TBPO > TPPO > TPAsO for ^{228}Ra

TBP > DEHPA > TPPO > TBPO > TOPO > TPAsO for ^{238}U

TOPO > TBPO > TBP > DEHPA > TPAsO > TPPO for ^{210}Pb

TBP > DEHPA > TOPO > TBPO > TPAsO > TPPO for ^{40}K

Also, our team examined and evaluated two surfactants as extracting agent for the removal of radium species from TE-NORM sludge produced from petroleum industry. In this investigation, cationic and nonionic surfactants were used as extracting agents for the removal of radium radionuclides from the sludge waste. Two surfactants namely cetyltrimethylammonium bromide (CTAB) and Triton X-100 (TX100) were investigated as the extracting agents. Different parameters affecting the removal of both ^{226}Ra and ^{228}Ra by the two surfactants as well as their admixture were studied by the batch technique [64]. The influence of contact time on dissolution/desorption of radium radionuclides (^{226}Ra , ^{228}Ra) from TE-NORM sludge waste using TX100 and CTAB surfactants was investigated. Transport and mass transfers of radium isotopes from the sludge might be a key process responsible for reducing radium from the sludge. To achieve maximum radium species removal, a specific period of time is required. The obtained results are represented in Table 9. It is obvious that the removal efficiency of radium isotopes is increased as the shaking time was increased and reach maximum after 60 minutes. The highest removal efficiency for ^{226}Ra was obtained using CTAB surfactant, and using TX100 surfactant for ^{228}Ra . However, further increase in the time of experiment leads to decrease of the removal efficiency [64].

Time, min	TX100 solution		CTAB solution	
	^{226}Ra (R, %)	^{228}Ra (R, %)	^{226}Ra (R, %)	^{228}Ra (R, %)
15	16.0 \pm 1.3	17.0 \pm 1.4	20.4 \pm 1.8	15.0 \pm 1.3
30	22.0 \pm 1.5	20.5 \pm 1.8	22.7 \pm 2.0	18.2 \pm 1.6
60	25.0 \pm 1.7	27.0 \pm 2.1	26.0 \pm 2.0	22.0 \pm 1.3
120	15.7 \pm 1.3	24.0 \pm 2.2	23.7 \pm 2.1	23.7 \pm 2.0
240	8.2 \pm 0.8	18.5 \pm 1.6	4.2 \pm 0.4	16.7 \pm 1.5

Table 9. Effect of contact time on the removal efficiency (R, %) of ^{226}Ra and ^{228}Ra using 1% (w/v) surfactants solutions

Effect of surfactant concentration on the extraction of radium isotopes is regarded as an important parameter affecting the removal of radium isotopes from TE-NORM sludge waste. The removal efficiency of radium species for both surfactant solutions increased with increasing surfactant concentration up to 1%. At higher surfactants concentration, a slight decrease was observed in Table 10. The optimum concentrations are found to be 1% for both surfactants

solutions. The effective removal of radium species from TE-NORM sludge can be explained by the increased solubility of radium species in the surfactant micelles. Generally, the change in the concentration of surfactant leads to change in its physical properties such as micelles formation and its solubilization effect for radium species or any contaminant (organic or inorganic species) present in TE-NORM sludge waste [65]. Therefore, the optimum surfactants concentrations are 1% for this treatment to avoid introduction of excess surfactants into sludge and avoid decrease in the radium removal %.

Concentration%	TX100 solution		CTAB solution	
	²²⁶ Ra (R, %)	²²⁸ Ra (R, %)	²²⁶ Ra (R, %)	²²⁸ Ra (R, %)
0.25	13.5 ± 1.4	15.0 ± 1.3	12.5 ± 0.9	14.4 ± 1.3
0.5	17.1 ± 1.1	19.1 ± 1.5	22.7 ± 1.7	20.0 ± 2.0
1.0	25.0 ± 1.7	27.0 ± 2.2	26.0 ± 2.0	22.0 ± 1.3
2.0	11.9 ± 1.1	20.5 ± 1.9	24.9 ± 1.7	23.0 ± 2.2
4.0	9.8 ± 0.9	19.0 ± 1.5	16.9 ± 1.4	14.8 ± 1.3
8.0	9.0 ± 0.8	13.3 ± 1.2	6.8 ± 0.6	8.8 ± 0.9

Table 10. Effect of surfactants concentrations on the removal efficiency (R, %) of ²²⁶Ra and ²²⁸Ra

The effect of temperature on the surfactants is not straightforward [66]. So that, temperature of surfactant solutions used for removal of radium species is an important parameter in surfactant-aided sludge washing process, and the experiments have been investigated with concentration of 1% TX100 and CTAB at 25–60°C. The results in Table 11 showed that the removal of Ra-isotopes are increased with increasing temperature and the removal of Ra species reach a maximum at 60°C using both surfactants solutions. The increase of Ra species removal efficiency is due to the properties of surfactants, where an increase in temperature generally results in an increase in the extent of solubility. The cloud point phenomenon occurs when a surfactant above its CMC causes the separation of the original solution into two phases when heated at a characteristic temperature called cloud point temperature. At this temperature, surfactant is no longer soluble in water and solution becomes hazy and cloudy. Above the cloud point, micelles formed from surfactant molecules act as an organic solvent in liquid–liquid extraction and the analytes are partitioned between the micelles and the aqueous phases [67]. It has been mentioned that the cloud point extraction procedure not only effectively solubilizes and concentrates pollutants but also appears to offer a means to further the concentrated surfactant-enhanced wash solutions that have been used in soil treatment processes [68]. About 25% of the radium species were initially removed from the TE-NORM sludge by solubilization in surfactants solution. About 55–60% removal was achieved upon the temperature raise to 60°C as shown in Table 11.

Synergism in surfactants may be defined as any situation where mixtures of surfactants have superior properties when compared to the properties of any of the single surfactant alone [69].

Temperature °C	TX100 solution		CTAB solution	
	^{226}Ra (R, %)	^{228}Ra (R, %)	^{226}Ra (R, %)	^{228}Ra (R, %)
25	25.0 ± 1.7	27.0 ± 2.2	26.0 ± 1.9	22.0 ± 1.3
35	30.0 ± 1.9	39.5 ± 2.2	28.6 ± 2.2	35.9 ± 2.8
45	53.0 ± 1.7	45.3 ± 2.0	43.5 ± 2.7	46.2 ± 3.4
60	58.6 ± 2.1	54.3 ± 3.3	49.8 ± 3.8	50.7 ± 4.2

Table 11. Effect of temperature on the removal efficiency (R, %) of ^{226}Ra and ^{228}Ra using surfactants solutions

There is usually a synergy effect for the CMC of surfactant mixtures (mixture of nonionic and ionic surfactant) [69]. Mixture of TX100 and CTAB surfactants showed synergistic interactions, which can be manifested as enhanced surface properties, spreading, and many other phenomena, as shown in Figure 5. The synergistic behavior of mixed surfactant systems can be exploited to reduce the total amount of surfactant used in a particular application resulting in the reduction of cost [70]. It was observed that the removal values of radium isotopes of mixed systems of both surfactants are higher than their corresponding values without mixing, which indicate synergistic interaction in mixed CTAB-TX100 as a chemical extraction system. Removal of 84% and 80% for ^{226}Ra and ^{228}Ra , respectively, are obtained using synergistic effect of 1% aqueous solution containing 1:1 of the two surfactants investigated. In other words, mixed micelle formation in aqueous solution can be greater than that of the individual surfactant, and explained by non-ideal solution theory [70]. Also, it was observed that combined extraction of cationic and nonionic surfactants was effective in removal of both ^{226}Ra and ^{228}Ra . Experiments indicated that removal efficiency was optimized (80–84%) when a mixture of 1% CTAB and 1% TX100 was employed at the ratio 1:1. The theoretical justification for this surfactants solution is based upon two hypotheses, first that surfactant micelles may sequester radium radionuclides which are sorbed to the TE-NORM sludge waste, and second that the surfactant micelles may increase the concentration of radium radionuclides in the aqueous phase. The developed chemical treatment process would enable to design an appropriate TE-NORM sludge washing strategy.

Glossary

Brief explanations of few terms are mentioned in the state-of-the-art in this short glossary.

NORM: Naturally occurring radioactive material.

TE-NORM: Technologically enhanced naturally occurring radioactive materials.

by-product: Any product from an (industrial) process that is not the intended primary product, but inevitable given the process implemented.

Product: The intended output from an (industrial) process.

REE: Rare earth elements (or lanthanides), comprising 16 chemical elements, including those with atomic numbers 57 (lanthanum) through 71 (lutetium), as well as yttrium (atomic number 39).

Waste: Any material that is:

- (a) The unwanted/substandard output from an (industrial) process that cannot be utilized under given circumstances (technological/economic perspective);
- (b) Declared as unwanted and/or unusable (regulatory perspective).

Scale: Solid deposit of low-solubility sulfates or carbonates on the inside of components of gas and oil production installations.

Sludge: Mixture of organic and mineral solids in water and liquid hydrocarbons separated from oil or gas at production facilities.

Radioactive material: Material designated in national law or by a regulatory body as being subject to regulatory control because of its radioactivity.

Half-life: For a radionuclide, the time required for the activity to decrease, by a radioactive decay process, by half. i.e., lose 50% of its activity.

Secular equilibrium: is a steady-state condition in which the rate of formation of the radioactive daughter products is just equal to the rate of decay; that is, the activity of radioactive parent and daughter are the same.

Separator: A pressure vessel used for separating well fluids produced from oil and gas wells into gaseous and liquid components.

Industrial process: This term is used very broadly in the present report to denote any human activity involving the application of technology, for example, the mining, processing, and drinking water treatment industries.

EPA: Environmental Protection Agency

UNSCEAR: United Nations Scientific Committee on the Effects of Atomic Radiation

TBP: Tri butyl phosphate

DEHPA: Bis (2-ethylhexyl phosphoric acid)

TOPO: Tri octyl phosphine oxide

TBPO: Tri Butyl phosphine oxide

TPAsO: Tri phenyl arsine oxide

TPPO: Tri phenyl phosphine oxide

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